

PROCEEDINGS  
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NATIONAL ACADEMY OF SCIENCES  
INDIA  
1952

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Parts III-VI

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Volume 21

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# PROCEEDINGS

## OF THE

# NATIONAL ACADEMY OF SCIENCES

## INDIA

### (SECTION A)

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### ON SOME INFINITE INTEGRALS INVOLVING STRUVE'S FUNCTIONS

BY SNEHLATA

*Department of Mathematics, Allahabad University*

(Communicated by Dr. P. L. Srivastava, Allahabad University)

1. The object of this paper is to evaluate a few infinite integrals involving Struve's function and the function  $\Phi_\nu(x)$  defined by

$$\Phi_\nu(x) = \sum_{s=0}^{\infty} \frac{(-1)^s x^{\nu+2s} \Gamma(s + \frac{1}{2})}{2^{\nu+2s} \Gamma(s+1) \Gamma(\nu+s+1)}, \quad (1.1)$$

$$R(\nu) > -1.$$

Struve's function is defined by

$$H_\mu(x) = \sum_{r=0}^{\infty} \frac{(-1)^r x^{\mu+2r+1}}{2^{\mu+2r+1} \Gamma(\mu+r+3/2) \Gamma(r+3/2)} \quad (1.2)$$

It is proposed throughout that the constants  $a$ ,  $b$  and  $c$  are *positive* and the parameters  $\nu$ ,  $\mu$ ,  $\lambda$ ,  $p$  are, for simplicity, supposed real; the formulæ are, however, valid in suitably chosen complex domains of both constants and parameters.

2. Let

$$I = \int_0^\infty x^{p-1} \cdot e^{-\frac{1}{2}cx^2} H_\mu(bx) \phi_\nu(ax) dx, \quad \nu + \mu + p + 1 > 0,$$



so that

$$\begin{aligned}
 I &= \int_0^{\infty} x^{\rho-1} \cdot e^{-\frac{1}{4}c^2x^2} \sum_{r=0}^{\infty} \frac{(-1)^r \left(\frac{bx}{2}\right)^{\mu+2r+1}}{\Gamma(\mu+r+3/2) \Gamma(r+3/2)} \\
 &\quad \times \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{ax}{2}\right)^{\nu+2s} \Gamma(s+\frac{1}{2})}{\Gamma(s+1) \Gamma(\nu+s+1)} dx, \\
 &= \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} \frac{(-1)^{r+s} \left(\frac{b}{2}\right)^{\mu+2r+1} \left(\frac{a}{2}\right)^{\nu+2s} \Gamma(s+\frac{1}{2})}{\Gamma(s+1) \Gamma(\nu+s+1) \Gamma(\mu+r+3/2) \Gamma(r+3/2)} \\
 &\quad \times \int_0^{\infty} x^{\rho+\mu+\nu+2r+2s} \cdot e^{-\frac{1}{4}c^2x^2} dx,
 \end{aligned}$$

the inversion of summation and integration being easily justifiable.

Then

$$\begin{aligned}
 I &= \frac{2^{\rho-1} b^{\mu+1} a^{\nu}}{c^{\rho+\mu+\nu+1}} \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} \frac{(-1)^{r+s} \left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s} \Gamma(s+\frac{1}{2})}{\Gamma(s+1) \Gamma(\nu+s+1) \Gamma(\mu+r+3/2)} \\
 &\quad \times \frac{\Gamma(\frac{1}{2} + \frac{1}{2}p + \frac{1}{2}\nu + \frac{1}{2}\mu + r + s)}{\Gamma(r+3/2)},
 \end{aligned}$$

where

$$R(\tfrac{1}{2} + \tfrac{1}{2}p + \tfrac{1}{2}\nu + \tfrac{1}{2}\mu) > 0.$$

Thus, we have, for  $R(\nu + \mu + p + 1) > 0$ ,

$$\begin{aligned}
 &\int_0^{\infty} x^{\rho-1} \cdot e^{-\frac{1}{4}c^2x^2} \phi_{\nu}(ax) H_{\mu}(bx) dx \\
 &= \frac{2^{\rho-1} a^{\nu} b^{\mu+1}}{c^{\rho+\mu+\nu+1}} \cdot \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} (-1)^{r+s} \\
 &\quad \times \frac{\left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s} \Gamma(s+\frac{1}{2}) \Gamma(\frac{1}{2} + \frac{1}{2}p + \frac{1}{2}\nu + \frac{1}{2}\mu + r + s)}{\Gamma(s+1) \Gamma(s+\nu+1) \Gamma(r+3/2) \Gamma(\mu+r+3/2)}.
 \end{aligned}$$

## 3. Particular Cases—

(i)  $p = 1$ .

$$\int_0^{\infty} e^{-\frac{1}{2}c^2x^2} \phi_{\nu}(ax) H_{\mu}(bx) dx = \frac{a^{\nu}b^{\mu+1}}{c^{\mu+\nu+2}} \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} (-1)^{r+s} \\ \times \frac{\left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s} \Gamma\left(1 + \frac{\nu}{2} + \frac{\mu}{2} + r + s\right) \Gamma\left(s + \frac{1}{2}\right)}{\Gamma(s+1) \Gamma(\nu + s + 1) \Gamma(r + 3/2) \Gamma(\mu + r + 3/2)},$$

where

$$R(\nu + \mu) > -2.$$

(a)  $\nu = -\frac{1}{2}$ .

Using the formula

$$\phi_{-\frac{1}{2}}(x) = \left(\frac{2}{x}\right)^{\frac{1}{2}} \cdot e^{-\frac{1}{2}x^2}, \quad (\text{A})$$

we get

$$\int_0^{\infty} e^{-\frac{1}{2}(c^2+a^2)x^2} \cdot x^{-\frac{1}{2}} H_{\mu}(bx) dx = \frac{b^{\mu+1}}{\sqrt{2} \cdot c^{\mu+\frac{3}{2}}} \cdot \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} (-1)^{r+s} \\ \times \frac{\left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s} \Gamma\left(\frac{3}{4} + \frac{\mu}{2} + r + s\right)}{\Gamma(s+1) \Gamma(r + 3/2) \Gamma(\mu + r + 3/2)},$$

where

$$R(\mu) > -3/2$$

(b)  $\nu = \mu = -\frac{1}{2}$ .

Using (A) and the formula

$$H_{-\frac{1}{2}}(x) = \sqrt{\frac{2}{\pi x}} \sin x, \quad (\text{B})$$

we get

$$\int_0^{\infty} x^{-1} e^{-\frac{1}{2}(c^2+a^2)x^2} \sin bx dx = \frac{\sqrt{\pi} b}{2c} \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} \frac{(-1)^{r+s} \left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s}}{\Gamma(s+1) \Gamma(r + 3/2)} \\ \times \frac{\Gamma\left(\frac{1}{2} + r + s\right)}{\Gamma(r+1)}.$$

(c)  $\mu = \frac{1}{2}$ .

Using the formula

$$H_{\frac{1}{2}}(x) = \sqrt{\frac{2}{\pi x}} (1 - \cos x), \quad (C)$$

we get

$$\int_0^{\infty} e^{-\frac{1}{2}c^2x^2} \cdot x^{-\frac{1}{2}} (1 - \cos bx) \phi_{\nu}(ax) dx = \frac{\sqrt{\pi} a^{\nu} b^2}{\sqrt{2} c^{\nu+5/2}} \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} \frac{(-1)^{r+s} \left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s} \Gamma(s + \frac{1}{2}) \Gamma\left(\frac{5}{4} + \frac{\nu}{2} + r + s\right)}{\Gamma(s+1) \Gamma(\nu+s+1) \Gamma(r+3/2) \Gamma(r+2)},$$

where

$$R(\nu) > -5/2.$$

Putting  $\nu = -\frac{1}{2}$  in this formula and using (A) we get

$$\int_0^{\infty} e^{-\frac{1}{2}(c^2+a^2)x^2} x^{-1} (1 - \cos bx) dx = \frac{\sqrt{\pi} \cdot b^2}{2 c^2} \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} (-1)^{r+s} \times \frac{\left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s} \Gamma(1+r+s)}{\Gamma(s+1) \Gamma(r+3/2) \Gamma(r+2)}.$$

(ii)  $p = \mu + 2$ .

$$\int_0^{\infty} x^{1+\mu} \cdot e^{-\frac{1}{2}(c^2x^2)} \phi_{\nu}(ax) H_{\mu}(bc) dx = \frac{b^{\mu+1} \cdot a^{\nu} \cdot 2^{\mu+1}}{c^{\nu+2\mu+3}} \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} (-1)^{r+s} \times \frac{\left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s} \Gamma\left(\frac{3}{2} + \frac{\nu}{2} + \mu + r + s\right) \Gamma(s + \frac{1}{2})}{\Gamma(s+1) \Gamma(\nu+s+1) \Gamma(r+3/2) \Gamma(\mu+r+3/2)},$$

where

$$R(\nu + 2\mu) > -3.$$

In particular, putting  $\mu = \frac{1}{2}$  and using (C) we have

$$\int_0^{\infty} x e^{-\frac{1}{2}c^2x^2} (1 - \cos bx) \phi_{\nu}(ax) dx = \frac{2 \sqrt{\pi} b^2 a^{\nu}}{c^{\nu+4}} \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} (-1)^{r+s} \times \frac{\left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s} \Gamma(s + \frac{1}{2}) \Gamma\left(2 + \frac{\nu}{2} + r + s\right) \Gamma(s + \frac{1}{2})}{\Gamma(s+1) \Gamma(\nu+s+1) \Gamma(r+3/2) \Gamma(r+2)},$$

where

$$R(\nu) > -4.$$

$$(iii) \quad p = 2 - \nu.$$

$$\begin{aligned} \int_0^\infty x^{1-\nu} e^{-\frac{1}{4}c^2x^2} \phi_\nu(ax) H_\mu(bx) dx &= \frac{b^{\mu+1} a^\nu}{2^{\nu-1} c^{\mu+3}} \cdot \sum_{r=0}^\infty \sum_{s=0}^\infty (-1)^{r+s} \\ &\times \frac{\left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s} \Gamma\left(\frac{3}{2} + \frac{\mu}{2} + r + s\right) \Gamma\left(s + \frac{1}{2}\right)}{\Gamma(s+1) \Gamma(\nu+s+1) \Gamma(r+3/2) \Gamma(\mu+r+3/2)}, \end{aligned}$$

where

$$R(\mu) > -3.$$

$$(iv) \quad \nu = \mu - \frac{1}{2}.$$

Using the formulæ (A) and (B) we get

$$\begin{aligned} \int_0^\infty x^{\rho-2} \cdot e^{-\frac{1}{4}(c^2+a^2)x^2} \sin(bx) dx &= \frac{2^{\rho-2} \sqrt{\pi} \cdot b}{c^\rho} \sum_{r=0}^\infty \sum_{s=0}^\infty (-1)^{r+s} \\ &\times \frac{\left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s} \Gamma\left(\frac{\rho}{2} + r + s\right)}{\Gamma(s+1) \Gamma(r+3/2) \Gamma(r+1)}, \end{aligned}$$

where

$$R(p) > 0.$$

$$(v) \quad \mu = \frac{1}{2}.$$

Using the formula (C) we get

$$\begin{aligned} \int_0^\infty x^{\rho-3/2} \cdot e^{-\frac{1}{4}c^2x^2} \cdot (1 - \cos bx) \phi_\nu(ax) dx &= \frac{b^2 a^\nu \cdot 2^{\rho-3/2}}{c^{\rho+\nu+3/2}} \\ &\times \sum_{r=0}^\infty \sum_{s=0}^\infty \frac{(-1)^{r+s} \left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s} \Gamma\left(\frac{3}{4} + \frac{\nu}{2} + \frac{\rho}{2} + r + s\right) \Gamma\left(s + \frac{1}{2}\right)}{\Gamma(s+1) \Gamma(\nu+s+1) \Gamma(r+3/2) \Gamma(r+2)}, \end{aligned}$$

where

$$R(\nu + p) > -3/2.$$

4. Let

$$I = \int_0^{\infty} x^{\rho-1} e^{-\frac{1}{4}c^2x^2} H_{\mu}(bx) \phi_{\nu}(ax) \phi_{\lambda}(ax) dx.$$

On using (1.1) and (1.2) we get

$$\begin{aligned} I &= \int_0^{\infty} x^{\rho-1} e^{-\frac{1}{4}c^2x^2} \sum_{r=0}^{\infty} \frac{(-1)^r \left(\frac{bx}{2}\right)^{\mu+2r+1}}{\Gamma(\mu+r+3/2) \Gamma(r+3/2)} \\ &\quad \times \sum_s \frac{(-1)^s \left(\frac{ax}{2}\right)^{\nu+2s} \Gamma(s+\frac{1}{2})}{\Gamma(s+1) \Gamma(\nu+s+1)} \sum_{q=0}^{\infty} \frac{(-1)^q \left(\frac{ax}{2}\right)^{\lambda+2q} \Gamma(q+\frac{1}{2})}{\Gamma(q+1) \Gamma(\lambda+q+1)} dx \\ &= \frac{2^{\rho-1} b^{\mu+1} a^{\nu+\lambda}}{c^{\rho+\nu+\mu+\lambda+1}} \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} \sum_{q=0}^{\infty} \frac{(-1)^{r+s+q} \left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2s+2q}}{\Gamma(r+3/2) \Gamma(\mu+r+3/2)} \\ &\quad \times \frac{\Gamma(s+\frac{1}{2}) \Gamma(q+\frac{1}{2}) \Gamma(\frac{1}{2}+\frac{1}{2}\rho+\frac{1}{2}\nu+\frac{1}{2}\mu+\frac{1}{2}\lambda+r+s+q)}{\Gamma(s+1) \Gamma(q+1) \Gamma(\nu+s+1) \Gamma(\mu+q+1)}, \end{aligned}$$

provided that

$$R(\rho + \nu + \mu + \lambda) > -1.$$

5. Generalising the result we get

$$\begin{aligned} &\int_0^{\infty} x^{\rho-1} e^{-\frac{1}{4}c^2x^2} H_{\mu}(bx) \phi_{\nu_1}(ax) \phi_{\nu_2}(ax) \dots \phi_{\nu_{n-1}}(ax) \phi_{\nu_n}(ax) dx \\ &= \frac{2^{\rho-1} b^{\mu+1} a^{\nu_1+\nu_2+\dots+\nu_{n-1}+\nu_n}}{c^{\rho+\mu+\nu_1+\nu_2+\dots+\nu_{n-1}+\nu_n+1}} \sum_{r=0}^{\infty} \sum_{r_1=0}^{\infty} \sum_{r_2=0}^{\infty} \dots \sum_{r_{n-1}=0}^{\infty} \sum_{r_n=0}^{\infty} \\ &\quad \frac{(-1)^{r+r_1+r_2+\dots+r_{n-1}+r_n}}{\Gamma(r+3/2) \Gamma(\mu+r+3/2)} \\ &\quad \times \frac{\left(\frac{b}{c}\right)^{2r} \left(\frac{a}{c}\right)^{2(r_1+r_2+\dots+r_{n-1}+r_n)} \Gamma(r_1+\frac{1}{2}) \Gamma(r_2+\frac{1}{2}) \dots \Gamma(r_{n-1}+\frac{1}{2}) \Gamma(r_n+\frac{1}{2})}{r_1! r_2! \dots r_{n-1}! r_n! \Gamma(\nu_1+r_1+1) \Gamma(\nu_2+r_2+1) \dots} \\ &\quad \times \frac{\Gamma(\frac{1}{2}+\frac{1}{2}\rho+\frac{1}{2}\mu+\frac{1}{2}\nu_1+\frac{1}{2}\nu_2+\dots+\frac{1}{2}\nu_{n-1}+\frac{1}{2}\nu_n+r+r_1+r_2+\dots+r_{n-1}+r_{n-1})}{\Gamma(\nu_{n-1}+\nu_{n-1}+1) \Gamma(\nu_n+r_n+1)}, \end{aligned}$$

provided that

$$R(p_\nu + \mu + \nu_1 + \nu_2 + \dots + \nu_n) > -1.$$

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Thanks are due to Prof. B. Mohan, M.A., Ph.D., Mathematics Department, Banaras Hindu University, for his valuable suggestions in preparing this paper. The author also expresses her indebtedness to Prof. P. L. Srivastava, M.A., D.Phil., Mathematics Department, Allahabad University, for his keen interest and guidance in this work.

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# ON SOME INFINITE INTEGRALS INVOLVING BESSEL FUNCTIONS

BY SNEHLATA

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(Communicated by Dr. P. L. Srivastava)

1. The object of this paper is to evaluate a few infinite integrals involving products of Bessel functions and the function  $\phi_\nu$  defined by

$$\phi_\nu(x) = \sum_0^\infty \frac{(-1)^r \Gamma(\frac{1}{2} + r) x^{\nu+2r}}{2^{\nu+2r} \Gamma(1 + \nu + r) r!}, \quad R(\nu) > -1 \quad (1.1)$$

Now, we know that

$$\phi_\nu(x) = \frac{(\frac{1}{2}x)^\nu}{\Gamma(\nu + \frac{1}{2})} \int_0^1 u^{-\frac{1}{2}} (1-u)^{\nu-\frac{1}{2}} e^{-\frac{1}{2}x^2u} du, \quad (1.2)$$

and

$$J_\mu(x) = \sum_0^\infty \frac{(-1)^s (\frac{1}{2}x)^{\mu+2s}}{s! \Gamma(\mu + s + 1)}. \quad (1.3)$$

2. We proceed to evaluate the integral

$$\begin{aligned} I &= \int_0^\infty x^{\rho-1} \phi_\nu(ax) J_\mu(bx) dx \\ &= \frac{a^\nu}{2^\nu \Gamma(\nu + \frac{1}{2})} \cdot \int_0^\infty x^{\rho+\nu-1} \sum_0^\infty \frac{(-1)^s (\frac{1}{2}bx)^{\mu+2s}}{s! \Gamma(\mu + s + 1)} dx \\ &\quad \times \int_0^1 u^{-\frac{1}{2}} (1-u)^{\nu-\frac{1}{2}} e^{-\frac{1}{2}a^2x^2u} du, \end{aligned}$$

on using (1.2) and (1.3). Thus

$$\begin{aligned} I &= \frac{a^\nu b^\mu}{2^{\nu+\mu} \Gamma(\nu + \frac{1}{2})} \cdot \int_0^1 u^{-\frac{1}{2}} (1-u)^{\nu-\frac{1}{2}} du \int_0^\infty \sum_{s=0}^\infty \frac{(-1)^s (\frac{1}{2}b)^{2s}}{s! \Gamma(\mu + s + 1)} \\ &\quad \times x^{\rho+\nu+\mu+2s-1} e^{-\frac{1}{2}a^2x^2u} dx, \end{aligned}$$

$$I = \frac{a^\nu b^\mu}{2^{\nu+\mu} \Gamma(\nu + \frac{1}{2})} \int_0^1 u^{-\frac{1}{2}} (1-u)^{\nu-\frac{1}{2}} \cdot du \cdot \int_0^\infty \sum_{s=0}^\infty \frac{(-1)^s (\frac{1}{2}b)^{2s}}{s! \Gamma(\mu + s + 1)} \\ \times x^{\rho + \nu + \mu + 2s-1} e^{-\frac{1}{4}a^2x^2u} dx,$$

a process easily justifiable.

$$\text{Put } \frac{1}{4} a^2 x^2 u = t,$$

$$\text{i.e., } x = \frac{2t^{\frac{1}{2}}}{au^{\frac{1}{2}}}$$

$$\text{and } dx = \frac{dt}{at^{\frac{1}{2}} u^{\frac{1}{2}}}.$$

Thus, we have

$$\int_0^\infty x^{\rho + \nu + \mu + 2s-1} e^{-\frac{1}{4} a^2 x^2 u} dx \\ = \int_0^\infty \left( \frac{2t^{\frac{1}{2}}}{au^{\frac{1}{2}}} \right)^{\rho + \nu + \mu + 2s-1} e^{-t} \frac{dt}{at^{\frac{1}{2}} u^{\frac{1}{2}}}.$$

Therefore

$$I = \frac{a^\nu b^\mu}{2^{\nu+\mu} \Gamma(\nu + \frac{1}{2})} \cdot \int_0^1 \sum_{s=0}^\infty \frac{(-1)^s (\frac{1}{2}b)^{2s}}{s! \Gamma(\mu + s + 1)} \cdot u^{-\frac{1}{2}} \cdot (1-u)^{\nu-\frac{1}{2}} du \\ \times \frac{2^{\rho + \nu + \mu + 2s-1}}{a^{\rho + \nu + \mu + 2s}} \int_0^\infty t^{\frac{p}{2} + \frac{\nu}{2} + \frac{\mu}{2} + s-1} e^{-t} u^{-\frac{1}{2}(\rho + \nu + \mu + 2s)} dt \\ = \frac{2^{\rho-1} b^\mu}{a^{\rho+\mu} \Gamma(\nu + \frac{1}{2})} \int_0^1 \sum_{s=0}^\infty \frac{(-1)^s \left(\frac{b}{a}\right)^{2s} \Gamma\left(\frac{p}{2} + \frac{\nu}{2} + \frac{\mu}{2} + s\right)}{s! \Gamma(\mu + s + 1)} \\ \times u^{\frac{1}{2} - \frac{1}{2}\rho - \frac{1}{2}\nu - \frac{1}{2}\mu - s-1} \cdot (1-u)^{\nu+\frac{1}{2}-1} du \\ = \frac{2^{\rho-1} b^\mu}{a^{\rho+\mu} \Gamma(\nu + \frac{1}{2})} \cdot \sum_{s=0}^\infty \frac{(-1)^s \left(\frac{b}{a}\right)^{2s} \Gamma\left(\frac{p}{2} + \frac{\nu}{2} + \frac{\mu}{2} + s\right)}{s! \Gamma(\mu + s + 1)} \\ \times \beta \left\{ \left( \frac{1}{2} - \frac{p}{2} - \frac{\nu}{2} - \frac{\mu}{2} - s \right), \left( \nu + \frac{1}{2} \right) \right\}.$$



Since

$$\beta(p, q) = \frac{\Gamma(p) \Gamma(q)}{\Gamma(p+q)},$$

we have

$$I = \frac{2^{\rho-1} \cdot b^\mu}{a^{\rho+\mu}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{b}{a}\right)^{2s} \Gamma\left(\frac{p}{2} + \frac{\nu}{2} + \frac{\mu}{2} + s\right) \Gamma\left(\frac{1}{2} - \frac{p}{2} - \frac{\nu}{2} - \frac{\mu}{2} - s\right)}{s! \Gamma(\mu + s + 1) \Gamma\left(1 - \frac{p}{2} + \frac{\nu}{2} - \frac{\mu}{2} - s\right)}.$$

Hence, we have

$$\begin{aligned} \int_0^\infty x^{\rho-1} \phi_\nu(ax) J_\mu(bx) dx &= \frac{2^{\rho-1} b^\mu}{a^{\rho+\mu}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{b}{a}\right)^{2s}}{s! \Gamma(\mu + s + 1)} \\ &\times \frac{\Gamma\left(\frac{p}{2} + \frac{\nu}{2} + \frac{\mu}{2} + s\right) \Gamma\left(\frac{1}{2} - \frac{p}{2} - \frac{\nu}{2} - \frac{\mu}{2} - s\right)}{\Gamma\left(1 - \frac{p}{2} + \frac{\nu}{2} - \frac{\mu}{2} - s\right)}, \end{aligned}$$

provided that

$$R(a) > 0, \quad 0 < R(p + \mu + \nu) < 1.$$

### 3. Particular Cases—

(i)  $p = 1$ .

$$\begin{aligned} \int_0^\infty \phi_\nu(ax) J_\mu(bx) dx &= \frac{b^\mu}{a^{1+\mu}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{b}{a}\right)^{2s} \Gamma\left(\frac{\nu}{2} + \frac{\mu}{2} + \frac{1}{2} + s\right)}{s! \Gamma(\mu + s + 1)} \\ &\times \frac{\Gamma\left(-\frac{\nu}{2} - \frac{\mu}{2} - s\right)}{\Gamma\left(\frac{1}{2} - \frac{\mu}{2} + \frac{\nu}{2} - s\right)}, \end{aligned}$$

where

$$R(a) > 0, \quad -1 < R(\mu + \nu) < 0.$$

(a)  $\mu = 0$ .

$$\int_0^\infty \phi_\nu(ax) J_0(bx) dx = \frac{1}{a} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{b}{a}\right)^{2s} \Gamma\left(\frac{\nu}{2} + \frac{1}{2} + s\right) \Gamma\left(-\frac{\nu}{2} - s\right)}{\Gamma\left(\frac{1}{2} + \frac{\nu}{2} - s\right) \cdot (s!)^2},$$

where

$$R(a) > 0, \quad -1 < R(\nu) < 0.$$

Now, putting  $\nu = -\frac{1}{2}$  in this and using the formula

$$\phi_{-\frac{1}{2}}(x) = \left(\frac{2}{x}\right)^{\frac{1}{2}} \cdot e^{-\frac{1}{2}x^2}, \quad (\text{A})$$

we get

$$\int_0^{\infty} x^{-\frac{1}{2}} \cdot e^{-\frac{1}{2}a^2x^2} J_0(bx) dx = \frac{1}{\sqrt{2a}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{b}{a}\right)^{2s} \Gamma(s + \frac{1}{4})}{(s!)^2},$$

where  $R(a) > 0$ .

(b)  $\nu = 0$ .

$$\int_0^{\infty} \phi_0(ax) J_{\mu}(bx) dx = \frac{b^{\mu}}{a^{\mu+1}} \cdot \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{b}{a}\right)^{2s} \Gamma\left(\frac{\mu}{2} + \frac{1}{2} + s\right) \Gamma\left(-\frac{\mu}{2} - s\right)}{s! \Gamma(\mu + s + 1) \Gamma\left(\frac{1}{2} - \frac{\mu}{2} - s\right)},$$

where  $R(a) > 0, \quad -1 < R(\mu) < 0$ .

(ii)  $p = \nu$ .

$$\begin{aligned} \int_0^{\infty} x^{\nu-1} \phi_{\nu}(ax) J_{\mu}(bx) dx &= \frac{2^{\nu-1} \cdot b^{\mu}}{a^{\nu+\mu}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{b}{a}\right)^{2s}}{s! \Gamma(\mu + s + 1)} \\ &\times \frac{\Gamma\left(\nu + \frac{\mu}{2} + s\right) \Gamma\left(\frac{1}{2} - \nu - \frac{\mu}{2} - s\right)}{\Gamma\left(1 - \frac{\mu}{2} - s\right)}, \end{aligned}$$

where  $0 < R(\mu + 2\nu) < 1, \quad R(a) > 0$ .

(a)  $\nu = -\frac{1}{2}$ .

Using the formula (A) we get

$$\int_0^{\infty} x^{-2} \cdot e^{-\frac{1}{2}a^2x^2} J_{\mu}(bx) dx = \frac{b^{\mu}}{4a^{\mu-1}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{b}{a}\right)^{2s} \Gamma\left(\frac{\mu}{2} + s - \frac{1}{2}\right)}{s! \Gamma(\mu + s + 1)},$$

where  $R(a) > 0, \quad 1 < R(\mu) < 2$ .

(iii)  $p = \nu - 2$ .

$$\int_0^{\infty} x^{\nu-3} \phi_{\nu}(ax) J_{\mu}(bx) dx = \frac{b^{\mu} \cdot 2^{\nu-3}}{a^{\nu+\mu-2}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{b}{a}\right)^{2s}}{s!} \\ \times \frac{\Gamma\left(\nu + \frac{\mu}{2} + s - 1\right) \Gamma\left(\frac{3}{2} - \nu - \frac{\mu}{2} - s\right)}{\Gamma(\mu + s + 1) \Gamma\left(2 - \frac{\mu}{2} - s\right)},$$

where  $2 < R(\mu + 2\nu) < 3$ ,  $R(a) > 0$ .

Putting  $\nu = -\frac{1}{2}$  and using the formula (A) we get

$$\int_0^{\infty} x^{-4} e^{-\frac{1}{4}a^2x^2} J_{\mu}(bx) dx = \frac{b^{\mu}}{16a^{\mu-3}} \cdot \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{b}{a}\right)^{2s} \Gamma\left(\frac{\mu}{2} + s - \frac{3}{2}\right)}{s! \Gamma(\mu + s + 1)},$$

where  $R(a) > 0$ ,  $3 < R(\mu) < 4$ .

4. Let

$$I = \int_0^{\infty} x^{\rho-1} J_{\mu}(bx) J_{\lambda}(bx) \phi_{\nu}(ax) dx. \\ = \frac{a^{\nu} b^{\mu+\lambda}}{2^{\nu+\mu+\lambda} \Gamma(\nu + \frac{1}{2})} \cdot \int_0^{\infty} x^{\rho-1} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{1}{2}b\right)^{2s} \cdot x^{\mu+2s}}{s! \Gamma(\mu + s + 1)} \\ \times \sum_{q=0}^{\infty} \frac{(-1)^q \left(\frac{1}{2}b\right)^{2q} x^{\lambda+2q}}{q! \Gamma(\lambda + q + 1)} \cdot x^{\nu} \int_0^1 u^{-\frac{1}{2}} (1-u)^{\nu-\frac{1}{2}} e^{-\frac{1}{4}a^2x^2u} du dx.$$

Proceeding exactly as in (2) we get

$$I = \frac{b^{\mu+\lambda} \cdot 2^{\rho-1}}{a^{\rho+\mu+\lambda}} \sum_{s=0}^{\infty} \sum_{q=0}^{\infty} \frac{(-1)^{s+q} \left(\frac{b}{a}\right)^{2s+2q} \Gamma\left(\frac{\rho}{2} + \frac{\nu}{2} + \frac{\mu}{2} + \frac{\lambda}{2} + s + q\right)}{s! q! \Gamma(\mu + s + 1) \Gamma(\lambda + q + 1)} \\ \times \frac{\Gamma\left(\frac{1}{2} - \frac{\rho}{2} - \frac{\nu}{2} - \frac{\mu}{2} - \frac{\lambda}{2} - s - q\right)}{\Gamma\left(1 - \frac{\rho}{2} + \frac{\nu}{2} - \frac{\mu}{2} - \frac{\lambda}{2} - s - q\right)},$$

provided that

$$R(a) > 0, 0 < R(p + \nu + \mu + \lambda) < 1.$$

5. Generalising the result we get

$$\begin{aligned} & \int_0^\infty x^{\beta-1} J_{\mu_1}(bx) J_{\mu_2}(bx) \dots J_{\mu_{n-1}}(bx) J_{\mu_n}(bx) \phi_\nu(ax) dx \\ &= \frac{b^{\mu_1 + \mu_2 + \dots + \mu_{n-1} + \mu_n} \cdot 2^{\beta-1}}{a^{\beta + \mu_1 + \mu_2 + \dots + \mu_{n-1} + \mu_n}} \\ & \times \sum_{r_1=0}^\infty \sum_{r_2=0}^\infty \dots \sum_{r_{n-1}=0}^\infty \sum_{r_n=0}^\infty \frac{(-1)^{r_1 + r_2 + \dots + r_{n-1} + r_n}}{r_1! r_2! \dots r_{n-1}! r_n!} \\ & \times \frac{\left(\frac{b}{a}\right)^{2(r_1 + r_2 + \dots + r_{n-1} + r_n)} \Gamma\left(\frac{p}{2} + \frac{\nu}{2} + \frac{\mu_1}{2} + \frac{\mu_2}{2} + \dots + \frac{\mu_{n-1}}{2} + \frac{\mu_n}{2} + r_1 + r_2 + \dots + r_{n-1} + r_n\right)}{\Gamma(\mu_1 + r_1 + 1) \Gamma(\mu_2 + r_2 + 1) \dots \Gamma(\mu_{n-1} + r_{n-1} + 1) \Gamma(\mu_n + r_n + 1)} \\ & \times \frac{\Gamma\left(\frac{1}{2} - \frac{p}{2} - \frac{\nu}{2} - \frac{\mu_1}{2} - \frac{\mu_2}{2} - \dots - \frac{\mu_{n-1}}{2} - \frac{\mu_n}{2} - r_1 - r_2 - \dots - r_{n-1} - r_n\right)}{\Gamma\left(1 - \frac{p}{2} - \frac{\nu}{2} - \frac{\mu_1}{2} - \frac{\mu_2}{2} - \dots - \frac{\mu_{n-1}}{2} - \frac{\mu_n}{2} - r_1 - r_2 - \dots - r_{n-1} - r_n\right)}, \end{aligned}$$

provided that

$$R(a) > 0, 0 < R(p + \nu + \mu_1 + \mu_2 + \dots + \mu_n) < 1.$$

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# ON GENERALISATIONS OF STIELTJES TRANSFORM

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1. If

$$f(s) = \int_0^{\infty} e^{-st} \phi(t) dt,$$

where

$$\phi(s) = \int_0^{\infty} e^{-st} \psi(t) dt,$$

then

$$f(s) = \int_0^{\infty} \frac{\psi(t)}{s+t} dt, \tag{1.1}$$

and the last equation is known as Stieltjes transform.

If  $\psi(t) dt$  be replaced by  $da(t)$  a more general case of the eqn. (1.1) is obtained in the form

$$f(s) = \int_0^{\infty} \frac{da(t)}{s+t}. \tag{1.2}$$

2. A generalisation of Stieltjes transform may be given by taking  $f(s)$  to be the generalised Laplace transform of  $\phi(u)$  in the form as given by Saksena and  $\phi(s)$  to be the ordinary Laplace transform of  $\psi(u)$ .

The result can be put as

THEOREM 1.—If

$$f(s) = s^a \int_0^{\infty} (qsu)^{c-\frac{1}{2}} e^{-(b-\frac{1}{2}q)su} W_{k,m}(qsu) \phi(u) du$$

and

$$\phi(s) = \int_0^{\infty} e^{-su} \psi(u) du,$$

then

$$f(s) = s^{a-1} q^{-1} \int_0^\infty \psi(t) \frac{\Gamma(c+m+1) \Gamma(c-m+1)}{\Gamma(c-K+3/2)} \\ \times {}_2F_1 \left[ \begin{matrix} c+m+1, c-m+1 \\ c-k+3/2 \end{matrix}; 1 - \frac{p}{q} - \frac{t}{qs} \right] dt,$$

provided that  $R(c \pm m + 1) > 0$ ,  $R(\rho + 1) > 0$  and  $R(q) > 0$ , the behaviour of  $\psi(u)$  being given by

$$\left. \begin{aligned} \psi(u) &= 0(u^\rho) \text{ for small } u \\ &= 0(e^{-u^\nu}) \text{ for large } u \end{aligned} \right\}, \quad R(\nu) > 0.$$

*Proof.*—We have

$$f(s) = s^a \int_0^\infty (qsu)^{c-\frac{1}{2}} e^{-(\frac{p}{2}-\frac{1}{2}q)su} W_{k,m}(qsu) \phi(u) du \quad (2.1)$$

and

$$\phi(u) = \int_0^\infty e^{-ut} \psi(t) dt. \quad (2.2)$$

Substituting for  $\phi(u)$  from (2.2) in (2.1) we get

$$f(s) = s^a \int_0^\infty (qsu)^{c-\frac{1}{2}} e^{-(\frac{p}{2}-\frac{1}{2}q)su} W_{k,m}(qsu) \int_0^\infty e^{-ut} \psi(t) dt du \\ = s^{a+c-\frac{1}{2}} \cdot q^{c-\frac{1}{2}} \int_0^\infty \int_0^\infty u^{c-\frac{1}{2}} e^{-(\frac{p}{2}-\frac{1}{2}q+\frac{t}{s})us} W_{k,m}(qsu) \psi(t) dt du \\ = s^{a+c-\frac{1}{2}} \cdot q^{c-\frac{1}{2}} \int_0^\infty \psi(t) dt \cdot \int_0^\infty u^{c-\frac{1}{2}} e^{-(\frac{p}{2}-\frac{1}{2}q+\frac{t}{s})us} W_{k,m}(qsu) du, \quad (2.3)$$

on changing the order of integration.

Now integrating with the help of Goldstein's integral

$$\int_0^\infty x^{l-1} e^{-(a^2+\frac{1}{2})x} W_{k,m}(x) dx = \frac{\Gamma(l+m+\frac{1}{2}) \Gamma(l-m+\frac{1}{2})}{\Gamma(l-k+1)} \\ \times {}_2F_1 \left[ \begin{matrix} l+m+\frac{1}{2}, l-m+\frac{1}{2} \\ l-k+1 \end{matrix}; -a^2 \right],$$

where

$$R(l \pm m + \tfrac{1}{2}) > 0, \quad R(a^2 + 1) > 0,$$

we get

$$\begin{aligned}
 f(s) &= s^{a+c-\frac{1}{2}} \cdot q^{c-\frac{1}{2}} \int_0^\infty \psi(t) \cdot \frac{\Gamma(c+m+1) \Gamma(c-m+1)}{\Gamma(c-k+3/2)} \cdot \frac{1}{(qs)^{c+\frac{1}{2}}} \\
 &\quad \times {}_2F_1 \left[ \begin{matrix} c+m+1, c-m+1 \\ c-k+3/2 \end{matrix}; 1 - \frac{p}{q} - \frac{t}{qs} \right] dt \\
 &= s^{a-1} q^{-1} \int_0^\infty \psi(t) \frac{\Gamma(c+m+1) \Gamma(c-m+1)}{\Gamma(c-k+3/2)} \\
 &\quad \times {}_2F_1 \left[ \begin{matrix} c+m+1, c-m+1 \\ c-k+3/2 \end{matrix}; 1 - \frac{p}{q} - \frac{t}{qs} \right] dt, \quad (2.4)
 \end{aligned}$$

provided that  $R(c \pm m + 1) > 0$ ,  $R(q) > 0$  and  $R(\rho + 1) > 0$ .

In order to justify the change in the order of integration in (2.3) let

$$\chi(t) = \psi(t) \int_0^\infty u^{c-\frac{1}{2}} \cdot e^{-(\rho-\frac{1}{2}q+\frac{t}{s})us} W_{k,m}(qsu) du,$$

and

$$\beta(u) = u^{c-\frac{1}{2}} W_{k,m}(qsu) \int_0^A e^{-(\rho-\frac{1}{2}q+\frac{t}{s})us} \psi(t) dt,$$

where  $A$  is small.

Now  $\chi(t)$  is uniformly convergent in  $t \geq 0$ , if  $R(\rho) \geq 0$ ,

$$R(c \pm m + 1) > 0.$$

And  $\beta(u)$  is uniformly convergent in  $u \geq 0$ , if  $R(c \pm m) \geq 0$ ,  $R(\rho + 1) > 0$ .

Next, let us consider the integral

$$I = \int_T^\infty u^{c-\frac{1}{2}} W_{k,m}(qsu) \left| du \int_{T'}^\infty e^{-(\rho-\frac{1}{2}q+\frac{t}{s})us} \psi(t) dt \right|,$$

where  $T$  and  $T'$  are large.

It is easy to see that  $I$  does not exceed a constant multiple of

$$\int_T^\infty |q^k s^k u^{c+k-1} e^{-\rho su}| du \int_{T'}^\infty |e^{-ut-t^\nu}| dt,$$

which tends to zero provided that  $R(ps) > 0$  and  $R(\nu) > 0$ .

Hence the change in the order of integration is justified when

$$R(s) > 0, R(v) > 0, R(c \pm m) \geq 0, R(\rho) \geq 0.$$

By analytic continuation these conditions can be relaxed to those mentioned in the theorem.

*Corollary.*—If we put  $a = 0$ ,  $q = 1$ ,  $c = m$  and  $p = 1$  in (2.4) we get

$$f(s) = \frac{\Gamma(2m+1)}{s \Gamma(m-k+3/2)} \cdot \int_0^\infty {}_2F_1 \left[ \begin{matrix} 2m+1, 1 \\ m-k+3/2 \end{matrix}; -\frac{t}{s} \right] \psi(t) dt.$$

This is the first result obtained by Varma, R. S.

3. Another generalisation of Stieltjes transform can be given by taking  $f(s)$  to be the ordinary Laplace transform of  $\phi(u)$  and  $\phi(s)$  to be the generalised Laplace transform of  $\psi(u)$  in the form as given by Saksena.

The result can be put as

THEOREM 2.—If

$$f(s) = \int_0^\infty e^{-us} \phi(u) du \quad (3.1)$$

and

$$\phi(s) = s^a \int_0^\infty (qsu)^{c-\frac{1}{2}} e^{-(p-\frac{1}{2}q)su} W_{k,m}(qsu) \psi(u) du, \quad (3.2)$$

then

$$f(s) = q^{a-1} \int_0^\infty t^{a-1} \psi(t) \cdot \frac{\Gamma(c+m+a+1) \Gamma(c-m+a+1)}{\Gamma(c-k+a+3/2)} \\ \times {}_2F_1 \left[ \begin{matrix} c+m+a+1, c-m+a+1 \\ c-k+a+3/2 \end{matrix}; 1 - \frac{p}{q} - \frac{s}{qt} \right] dt, \quad (3.3)$$

provided that  $R(c \pm m + a + 1) > 0$ ,  $R(\rho + 1) > 0$ ,  $R(q) > 0$ , the behaviour of  $\psi(u)$  being given by

$$\left. \begin{aligned} \psi(u) &= 0(u^\rho) \text{ for small } u \\ &= 0(e^{-u^\rho}) \text{ for large } u \end{aligned} \right\}, R(v) > 0.$$

*Proof.*—Proceeding exactly in the same way as in Theorem 1, Theorem 2 can be easily proved.



*Corollary.*—If we put  $a = 0$ ,  $q = 1$ ,  $p = 1$ ,  $c = m$  in (3.3) we get

$$f(s) = \frac{\Gamma(2m+1)}{\Gamma(m-k+3/2)} \cdot \int_0^\infty (1/t) {}_2F_1 \left[ \begin{matrix} 2m+1, 1 \\ m-k+3/2 \end{matrix}; -\frac{s}{t} \right] \psi(t) dt,$$

which is the second result obtained by Varma, R. S.

4. Yet another generalisation of Stieltjes transform can be given by taking  $f(s)$  to be the generalised Laplace transform of  $\phi(u)$  in the form given by Meijer and Greenwood and  $\phi(s)$  to be the generalised Laplace transform of  $\psi(u)$  in the form given by Saksena. The result can be stated as

THEOREM 3.—If

$$f(s) = \sqrt{\frac{2s}{\pi}} \int_0^\infty u^{\frac{1}{2}} k_\nu(su) \phi(u) du$$

and

$$\phi(s) = s^a \int_0^\infty (qsu)^{c-\frac{1}{2}} e^{-(p-\frac{1}{2}q)su} W_{k,m}(qsu) \psi(u) du,$$

then

$$\begin{aligned} f(s) = & q^{c-\frac{1}{2}} \cdot \int_0^\infty t^{c-\frac{1}{2}} \psi(t) \sum_{r=0}^\infty \left[ \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-m-k)} \cdot \frac{(\frac{1}{2}+m-k)_r}{(2m+1)_r} (qt)^{m+r+\frac{1}{2}} \right. \\ & \times \frac{\Gamma(c+m+a+r-\nu+3/2)}{s^{c+m+a+r+1}} \frac{\Gamma(c+m+a+r+\nu+3/2)}{s^{c+m+a+r+1}} \\ & \times \frac{P_{\nu-\frac{1}{2}}^{-(c+m+a+r+1)}(\cosh a)}{\sinh^{c+m+a+r+1} a} \\ & + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}+m-k)} \frac{(\frac{1}{2}-m-k)_r}{(-2m+1)_r} (qt)^{-m+r+\frac{1}{2}} \\ & \times \frac{\Gamma(c-m+a+r-\nu+3/2)}{s^{c-m+a+r+1}} \frac{\Gamma(c-m+a+r+\nu+3/2)}{s^{c-m+a+r+1}} \\ & \left. \times \frac{P_{\nu-\frac{1}{2}}^{-(c-m+a+r+1)}(\cosh a)}{\sinh^{c-m+a+r+1} a} \right] dt, \end{aligned} \quad (4.1)$$

where

$$\cosh a = \frac{pt}{s},$$

provided that  $R(\beta) > 0$ ,  $R(s) > 0$ ,  $R(\rho + c + a \pm m + 1) > 0$ ,  
 $R(c + a \pm m \pm \nu + 3/2) > 0$  and

$$\left. \begin{aligned} \psi(u) &= 0(u^\rho) \text{ for small } u \\ &= 0(e^{-u^\beta}) \text{ for large } u \end{aligned} \right\}, R(\beta) > 0.$$

*Proof.*—We have

$$f(s) = \sqrt{\frac{2s}{\pi}} \int_0^\infty u^{\frac{1}{2}} k_\nu(su) \phi(u) du \quad (4.2)$$

and

$$\phi(u) = u^\alpha \int_0^\infty (qut)^{c-\frac{1}{2}} e^{-(\frac{1}{2}-\frac{1}{2}q)ut} \cdot W_{k,m}(qut) \psi(t) dt. \quad (4.3)$$

Substituting for  $\phi(u)$  from (4.3) in (4.2) we get

$$f(s) = \sqrt{\frac{2s}{\pi}} \int_0^\infty u^{\frac{1}{2}} k_\nu(su) u^\alpha \int_0^\infty (qut)^{c-\frac{1}{2}} e^{-(\frac{1}{2}-\frac{1}{2}q)ut} \\ \times W_{k,m}(qut) \psi(t) dt du.$$

On changing the order of integration, we get

$$f(s) = \sqrt{\frac{2s}{\pi}} q^{c-\frac{1}{2}} \cdot \int_0^\infty t^{c-\frac{1}{2}} \psi(t) dt \cdot \int_0^\infty u^{c+\alpha} e^{-(\frac{1}{2}-\frac{1}{2}q)ut} k_\nu(su) \\ \times W_{k,m}(qut) du.$$

On substituting the expression for  $W_{k,m}(qut)$  in terms of Kummer's function, we have

$$f(s) = \sqrt{\frac{2s}{\pi}} q^{c-\frac{1}{2}} \int_0^\infty t^{c-\frac{1}{2}} \psi(t) dt \cdot \int_0^\infty \sum_{r=0}^\infty \\ \left[ \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-m-k)} \cdot \frac{(\frac{1}{2}+m-k)_r}{(2m+1)_r \mathcal{L}^r} e^{-\frac{1}{2}qut} \right. \\ \times k_\nu(su) u^{c+\alpha+m+\frac{1}{2}+r} (qt)^{m+r+\frac{1}{2}} \\ \left. + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}+m-k)} \cdot \frac{(\frac{1}{2}-m-k)_r}{(-2m+1)_r \mathcal{L}^r} \right. \\ \left. \times e^{-\frac{1}{2}qut} k_\nu(su) u^{c+\alpha-m+r+\frac{1}{2}} (qt)^{-m+r+\frac{1}{2}} \right] du.$$

Now, from Watson, *Theory of Bessel Functions*, p. 388, we have

$$\int_0^{\infty} e^{-t \cosh \alpha} k_{\nu}(t) t^{\mu-1} dt = \sqrt{\frac{\pi}{2}} \cdot \Gamma(\mu - \nu) \Gamma(\mu + \nu) \times \frac{P_{\nu-\frac{1}{2}}^{\frac{1}{2}-\mu}}{\sinh^{\mu-\frac{1}{2}} \alpha} (\cosh \alpha),$$

where  $R(\mu) > |R(\nu)|$  and  $R(\cosh \alpha) > -1$ .

Therefore, integrating term by term with the help of the above result, which is valid since,

(1) the infinite series in the integral is uniformly convergent in the range  $u \geq 0$ ,

and

$\int_0^{\infty} |k_{\nu}(us)| du$  is convergent by virtue of [Watson, *Theory of Bessel Functions* p. 202]

$$k_{\nu}(z) \sim \sqrt{\frac{\pi}{2z}} e^{-z}$$

when  $z$  is large and  $|\arg z| < 3/2 \pi$ ,

we have

$$\begin{aligned} f(s) = q^{c-\frac{1}{2}} \int_0^{\infty} t^{c-\frac{1}{2}} \psi(t) \cdot \sum_{r=0}^{\infty} \left[ \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-m-k)} \frac{(\frac{1}{2}+m-k)_r}{(2m+1)_r} \frac{1}{t^r} \right. \\ \times (qt)^{m+r+\frac{1}{2}} \\ \times \frac{\Gamma(c+m+a+r-\nu+3/2)}{s^{c+m+a+r+1}} \frac{\Gamma(c+m+a+r+\nu+3/2)}{s^{c+m+a+r+1}} \\ \times \frac{P_{\nu-\frac{1}{2}}^{-(c+m+a+r+1)} (\cosh a)}{\sinh^{c+m+a+r+1} a} \\ + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}+m-k)} \frac{(\frac{1}{2}-m-k)_r}{(-2m+1)_r} \frac{1}{t^r} (qt)^{-m+r+\frac{1}{2}} \\ \times \frac{\Gamma(c-m+a+r+\nu+3/2)}{s^{c-m+a+r+1}} \frac{\Gamma(c-m+a+r+\nu+3/2)}{s^{c-m+a+r+1}} \\ \left. \times \frac{P_{\nu-\frac{1}{2}}^{-(c-m+a+r+1)} (\cosh a)}{\sinh^{c-m+a+r+1} a} \right] dt, \end{aligned}$$

provided that

$$R(\beta) > 0, \quad R(s) > 0, \quad R(\rho + c + a \pm m + 1) > 0,$$

$$R(c + a \pm m \pm \nu + 3/2) > 0.$$

The change in the order of integration can be easily justified as in Theorem 1.

*Corollary 1.*—If we put  $q = 1$ ,  $c = m$ ,  $p = 1$ ,  $a = 0$  in (4.1) we get

$$\begin{aligned} f(s) = & \int_0^\infty t^{m-\frac{1}{2}} \psi(t) \sum_{r=0}^\infty \left[ \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2} - m - k)} \frac{(\frac{1}{2} + m - k)_r}{(2m + 1)_r} \frac{t^{m+r+\frac{1}{2}}}{s^r} \right. \\ & \times \frac{\Gamma(2m + r - \nu + 3/2) \Gamma(2m + r + \nu + 3/2)}{s^{-2m+r+1}} \\ & \times \frac{P_{\nu-\frac{1}{2}}^{-2m-r-1} \left( \frac{t}{s} \right)}{\left( \frac{t^2}{s^2} - 1 \right)^{m+\frac{r+1}{2}}} \\ & + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2} + m - k)} \frac{(\frac{1}{2} - m - k)_r}{(-2m + 1)_r} \frac{t^{-m+r+\frac{1}{2}}}{s^r} \\ & \times \frac{\Gamma(r - \nu + 3/2) \Gamma(r + \nu + 3/2)}{s^{r+3/2}} \\ & \left. \times \frac{\left\{ P_{\nu-\frac{1}{2}}^{-r-1} \left( \frac{t}{s} \right) \right\}}{\left( \frac{t^2}{s^2} - 1 \right)^{\frac{r+1}{2}}} \right] dt, \end{aligned}$$

which is the result obtained by Saksena.

*Corollary.*—If we put  $a = 0$ ,  $q = 1$ ,  $p = 1$ ,  $c = m$  and  $k = \frac{1}{2} - m$  in (4.1), we get

$$f(s) = \frac{1}{s} \Gamma(3/2 + \nu) \Gamma(3/2 - \nu) \int_0^\infty \left( \frac{t^2}{s^2} - 1 \right)^{-\frac{1}{2}} P_{\nu-\frac{1}{2}}^{-1} \left( \frac{t}{s} \right) \psi(t) dt,$$

which reduces to the ordinary Stieltjes transform if we further put  $\nu = \frac{1}{2}$ .

5. Another generalisation of Stieltjes's transform can be given by taking  $f(s)$  to be the generalised Laplace transform of  $\phi(u)$  in the form given by

Saksena and  $\phi(s)$  to be the generalised Laplace transform of  $\psi(u)$  in the form given by Saksena. The result can be stated as

THEOREM 4.—If

$$f(s) = s^a \int_0^\infty (qsu)^{c-\frac{1}{2}} e^{-(\frac{1}{2}-\frac{q}{2})su} W_{k,m}(qsu) \phi(u) du$$

and

$$\phi(s) = s^a \int_0^\infty (qsu)^{d-\frac{1}{2}} e^{-(\frac{1}{2}-\frac{q}{2})su} W_{l,n}(qsu) \psi(u) du,$$

then

$$\begin{aligned} f(s) = & s^{a+c-\frac{1}{2}} q^{c+d-1} \int_0^\infty t^{d-\frac{1}{2}} \psi(t) \sum_{r=0}^\infty \left[ \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-k-m)} \frac{(\frac{1}{2}+m-k)_r}{(2m+1)_r} \frac{1}{z^r} \right. \\ & \times (qs)^{m+r+\frac{1}{2}} \cdot \frac{\Gamma(c+d+a+m+n+r+1)}{\Gamma(c+d+a+m+r-l+3/2)} \frac{\Gamma(c+d+a-m-n+r+1)}{(qt)^{c+d+a+m+r+\frac{1}{2}}} \\ & \times {}_2F_1 \left\{ \begin{matrix} c+d+a+m+n+r+1, & c+d+a-m-n+r+1; \\ c+d+a+m+r-l+3/2 \end{matrix} \right. \\ & \left. 1 - \frac{p}{q} - \frac{sp}{qt} \right\} \\ & + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}-k+m)} \frac{(\frac{1}{2}-m-k)_r}{(-2m+1)_r} \frac{1}{z^r} \\ & \times \frac{\Gamma(c+d+a-m+n+r+1)}{\Gamma(c+d+a-m+r-l+3/2)} \frac{\Gamma(c+d+a-m-n+r+1)}{(qt)^{c+d+a-m+r+\frac{1}{2}}} \\ & \times \frac{(qs)^{-m+r+\frac{1}{2}}}{(qt)^{c+d+a-m+r+\frac{1}{2}}} \\ & \times {}_2F_1 \left\{ \begin{matrix} c+d+a-m+n+r+1, & c+d+a-m-n+r+1; \\ c+d+a-m+r-l+3/2 \end{matrix} \right. \\ & \left. 1 - \frac{p}{q} - \frac{sp}{qt} \right\} dt, \end{aligned}$$

provided that  $R(c+d+a \pm m \pm n+1) > 0$ ,  $R(s) > 0$ ,  $R(q) > 0$ ,

$R(\rho+d \pm n+1) > 0$  and

$$\left. \begin{aligned} \psi(t) &= 0(t^\rho) \text{ for small } t \\ &= 0(e^{-t^\nu}) \text{ for larg } t \end{aligned} \right\}, R(\nu) > 0.$$

*Proof.*—Proceeding exactly in the same manner as in Theorem 1, Theorem 4 can be proved.

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# ON GENERALISED LAPLACE TRANSFORM AND SELF-RECIPROCAL FUNCTIONS

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1. In this paper it is proposed to obtain generalised Laplace transform of the function  $\phi(t)$  when  $t^\lambda \phi(t)$  is self-reciprocal\* in the Hankel transform of order  $\nu$ . Further, it is intended to consider the representation of functions which are  $R_\nu$  by means of generalised Laplace integrals of certain other functions. The corresponding results in sine and cosine transforms will so be considered.

THEOREM 1.—If

$$f(s) = s^a \int_0^\infty (qst)^{c-\frac{1}{2}} \cdot e^{-(p-\frac{1}{2}q)st} W_{k,m}(qst) \phi(t) dt,$$

and  $t^\lambda \phi(t)$  is self-reciprocal in the Hankel transform of order  $\nu$ , then, provided the integral is convergent,

$$f(s^\mu) = \int_0^\infty y^{\lambda+\frac{1}{2}} \cdot \mathcal{L}_\lambda^\mu(y/s^\mu) \phi(y) dy, \quad (\text{A})$$

where

$$\begin{aligned} \mathcal{L}_\lambda^\mu \left( \frac{y}{s^\mu} \right) &= s^{\mu(\lambda+a-3/2)} \cdot \frac{q^{\nu+\lambda-3/2}}{2^{-\nu}} \left( \frac{y}{4s^\mu} \right)^\nu \\ &\times \sum_{r=0}^\infty \frac{(-1)^r \Gamma(c+m+\nu-\lambda+2r+3/2) \Gamma(c-m+\nu-\lambda+2r+3/2)}{2^{-2r} \Gamma(c+\nu-\lambda+2r-k+2) q^{2r}} \\ &\times \left( \frac{y}{4s^\mu} \right)^{2r} {}_2F_1 \left[ \begin{matrix} c+m+\nu-\lambda+2r+3/2, c-m+\nu-\lambda+2r+3/2 \\ c+\nu-\lambda+2r-k+2 \end{matrix} ; 1-p/q \right], \end{aligned}$$

\* A function  $f(x)$  is called self-reciprocal in the Hankel transform of order  $\nu$ , if it satisfies the integral equation

$$f(x) = f \int_0^\infty \sqrt{xy} J_\nu(xy) f(y) dy.$$

Following Hardy and Titchmarsh we shall call such functions,  $R_\nu$ . If  $\nu = \mp \frac{1}{2}$ , the function is self-reciprocal in cosine or sine transform and is called  $R_c$  or  $R_s$ .

provided that

$$R(c \pm m + \nu - \lambda + 3/2) > 0, R(\nu + \alpha + \lambda + 3/2) > 0,$$

$$R(c \pm m + \alpha + 1) > 0, p > q, R(ps^\mu) > 0,$$

and

$$\left. \begin{aligned} \phi(x) &= 0(x^\alpha) \text{ for small } x \\ &= 0(e^{-x\beta}) \text{ for large } x \end{aligned} \right\}, R(\beta) > 0.$$

*Proof.*—Since

$$f(s) = s^\alpha \int_0^\infty (qst)^{c-\frac{1}{2}} \cdot e^{-(p-\frac{1}{2}q)st} \cdot W_{k,m}(qst) \phi(t) dt \quad (1.1)$$

and

$$t^\lambda \phi(t) = \int_0^\infty (ty)^{\frac{1}{2}} J_\nu(ty) y^\lambda \phi(y) dy, \quad (1.2)$$

$J_\nu$  denoting the Bessel function of order  $\nu$ .

If we use (1.2) in (1.1) after replacing  $s$  by  $s^\mu$ , we get

$$\begin{aligned} f(s^\mu) &= s^{\alpha\mu} \int_0^\infty (qs^\mu t)^{c-\frac{1}{2}} e^{-(p-\frac{1}{2}q)s^\mu t} \cdot W_{k,m}(qs^\mu t) \\ &\quad \times \int_0^\infty t^{-\lambda} \sqrt{ty} \cdot J_\nu(ty) y^\lambda \phi(y) dy dt \\ &= s^{\alpha\mu+c\mu-\frac{1}{2}\mu} q^{c-\frac{1}{2}} \int_0^\infty y^{\lambda+\frac{1}{2}} \phi(y) dy \int_0^\infty t^{c-\lambda} e^{-(p-\frac{1}{2}q)s^\mu t} \\ &\quad \times W_{k,m}(qs^\mu t) J_\nu(ty) dt, \end{aligned} \quad (1.3)$$

on changing the order of integration.

$$\begin{aligned} &= s^{\alpha\mu+c\mu-\frac{1}{2}\mu} q^{c-\frac{1}{2}} \cdot \int_0^\infty \sum_{r=0}^\infty \frac{(-1)^r (\frac{1}{2})^{\nu+2r}}{\Gamma(\nu+r+1)} y^{\lambda+\frac{1}{2}+\nu+2r} \phi(y) dy \\ &\quad \times \int_0^\infty t^{(c+\nu+2r-\lambda)} e^{-(p-\frac{1}{2}q)s^\mu t} \cdot W_{k,m}(qs^\mu t) dt, \end{aligned}$$

where

$$R(\nu + \lambda + \alpha + 3/2) > 0, R(c \pm m + \alpha + 1) > 0, R(s^\mu p) > 0, p > q$$

on substituting the expression of  $J_\nu(ty)$  as an infinite series and changing the order of integration and summation, which is permissible since,



(i)  $J_\nu(ty)$  is uniformly convergent in the arbitrary interval  $(0, A)$  of  $t$ ,

(ii)  $t^{c+\nu-\lambda} e^{-(p-\frac{1}{2}q)s^\mu t} W_{k,m}(qs^\mu t)$  is continuous for all finite  $t \geq 0$ , provided that

$$R(c + \nu - \lambda \pm m + \frac{1}{2}) \geq 0,$$

and

$$(iii) \int_0^\infty (qs^\mu t)^{c-\frac{1}{2}} t^{-\lambda+\frac{1}{2}} e^{-(p-\frac{1}{2}q)s^\mu t} \cdot W_{k,m}(qs^\mu t) J_\nu(ty) dt$$

is also convergent when

$$R(c \pm m + \nu - \lambda + 3/2) > 0, \text{ and } R(q) < R(p).$$

Now, integrating with the help of Goldstein's formula

$$\int_0^\infty x^{l-1} e^{-(a^2 + \frac{1}{2})x} W_{k,m}(x) dx = \frac{\Gamma(l + m + \frac{1}{2}) \Gamma(l - m + \frac{1}{2})}{\Gamma(l - k + 1)} \\ \times {}_2F_1 \left[ \begin{matrix} l + m + \frac{1}{2}, l - m + \frac{1}{2} \\ l - k + 1 \end{matrix} ; -a^2 \right],$$

where  $R(l \pm m + \frac{1}{2}) > 0$ ,  $R(a^2 + 1) > 0$ ,

we get

$$f(s^\mu) = s^{\alpha\mu+c\mu-\frac{1}{2}\mu} \cdot q^{c-\frac{1}{2}} \cdot \int_0^\infty \sum_{r=0}^\infty \frac{(-1)^r (\frac{1}{2})^{p+2r}}{\Gamma(r) \Gamma(\nu + r + 1)} y^{\lambda + \nu + 2r + \frac{1}{2}} \phi(y) \\ \times \frac{\Gamma(c + m + \nu - \lambda + 2r + 3/2) \Gamma(c - m + \nu - \lambda + 2r + 3/2)}{s^{\mu(c-\lambda+\nu+2r+1)} \Gamma(c + \nu - \lambda + 2r - k + 2) q^{c-\lambda+\nu+2r+1}} \\ \times {}_2F_1 \left[ \begin{matrix} c+m+\nu+2r-\lambda+3/2, c-m+\nu-\lambda+2r+3/2 \\ c + \nu - \lambda + 2r - k + 2 \end{matrix} ; 1 - p/q \right] dy, \quad (1.4)$$

where

$$R(c \pm m + \nu - \lambda + 3/2) > 0, R(\nu + \alpha + \lambda + 3/2) > 0,$$

$$R(c \pm m + \alpha + 1) > 0, R(s^\mu p) > 0, p > q.$$

This is the same as (A).

To justify the change in the order of integration in the step (1.3) let

$$\theta(y) = y^{\lambda+\frac{1}{2}} \phi(y) \int_0^\infty t^{c-\lambda} e^{-(p-\frac{1}{2}q)s^\mu t} \cdot W_{k,m}(qs^\mu t) J_\nu(ty) dt,$$

and

$$\chi(t) = t^{c-\lambda} e^{-(p-\frac{1}{2}q)s^\mu t} W_{k,m}(qs^\mu t) \int_0^\infty y^{\lambda+\frac{1}{2}} \phi(y) J_\nu(ty) dy$$

and

$$\left. \begin{aligned} \phi(x) &= 0(x^\alpha) \text{ for small } x \\ &= 0(e^{-x^\beta}) \text{ for large } x \end{aligned} \right\}, R(\beta) > 0. \quad (1.5)$$

Now  $\theta(y)$  converges uniformly for  $y \geq 0$ , if  $R(\lambda + \alpha + \nu + \frac{1}{2}) \geq 0$ ,  $R(c \pm m - \lambda + \nu + 3/2) > 0$ ,  $R(s^\mu p) > 0$ ,  $p > q$ , on account of the following behaviour of  $W_{k,m}(x)$

$$\left. \begin{aligned} W_{k,m}(x) &= 0(x^{\pm m + \frac{1}{2}}), \text{ when } x \text{ is small} \\ &= 0(x^k e^{-\frac{1}{2}x}) \text{ when } x \text{ is large} \end{aligned} \right\} \quad (1.6)$$

and the following behaviour of  $J_\nu(x)$

$$\left. \begin{aligned} J_\nu(x) &= 0(x^\nu) \text{ for small } x \\ &= 0(x^{-\frac{1}{2}}) \text{ for large } x \end{aligned} \right\} \quad (1.7)$$

And,  $\chi(t)$  converges uniformly for  $t \geq 0$ , if

$$R(c \pm m - \lambda + \nu + \frac{1}{2}) \geq 0, R(\lambda + \frac{1}{2} + \nu + \alpha + 1) > 0,$$

$$R(s^\mu p) > 0, p > q.$$

Again, if we consider the integral

$$\begin{aligned} I &= s^{a\mu + \mu c - \frac{1}{2}\mu} q^{c-\frac{1}{2}} \int_T^\infty |y^{\lambda+\frac{1}{2}} \phi(y)| dy \\ &\times \int_{T'}^\infty |t^{c-\lambda} e^{-(p-\frac{1}{2}q)s^\mu t} W_{k,m}(qs^\mu t) J_\nu(ty)| dt, \end{aligned}$$

where  $T$  and  $T'$  are large, we see, on account of the asymptotic behaviour of  $W_{k,m}(x)$  and  $J_\nu(x)$ , that  $I$  does not exceed a constant multiple of

$$s^{a\mu + \mu c - \frac{1}{2}\mu} q^{c-\frac{1}{2}} \int_T^\infty |y^\lambda e^{-y^\beta}| dy \int_{T'}^\infty |t^{c+k-\lambda-\frac{1}{2}} e^{-ps^\mu t}| dt,$$

which tends to zero when  $R(ps^\mu) > 0$ .

Hence the change in the order of integration is justified when

$$R(\nu + \alpha + \lambda + \tfrac{1}{2}) \geq 0, \quad R(c \pm m + \alpha + 1) > 0,$$

$$R(c \pm m + \nu - \lambda + \tfrac{1}{2}) \geq 0, \quad R(ps^\mu) > 0, \quad p > q.$$

Now,

$$f(s^\mu) = \int_0^\infty y^{\lambda+\frac{1}{2}} \phi(y) L_\lambda^\mu(y/s^\mu) dy,$$

where

$$\begin{aligned} L_\lambda^\mu \left( \frac{y}{s^\mu} \right) &= s^{\mu(\lambda+\alpha-3/2)} \cdot \frac{q^{\nu+\lambda-3/2}}{2^{-\nu}} \cdot \left( \frac{y}{4s^\mu} \right)^\nu \\ &\times \sum_{r=0}^{\infty} \frac{(-1)^r \Gamma(c+m+\nu-\lambda+2r+3/2) \Gamma(c-m+\nu-\lambda+2r+3/2)}{2^{-2r} \Gamma(c+\nu-\lambda+2r-k+2) q^{2r}} \\ &\times \left( \frac{y}{4s^\mu} \right)^{2r} {}_2F_1 \left[ \begin{matrix} c+m+\nu-\lambda+2r+3/2, & c-m+\nu-\lambda+2r+3/2 \\ c+\nu-\lambda+2r-k+2 \end{matrix} ; 1 - \frac{p}{q} \right]. \end{aligned}$$

2. *Properties of  $L_\lambda^\mu(t)$ , where  $t = \frac{y}{s^\mu}$ .*

The behaviour of  $L_\lambda^\mu(t)$  for small and large values of  $t$  can easily be investigated.

We have in fact

$$\begin{aligned} L_\lambda^\mu(t) &= \frac{s^{\mu(\lambda+\alpha-3/2)}}{2^\nu q^{3/2-\nu-\lambda}} \cdot t^\nu \cdot \sum_{r=0}^{\infty} \frac{\Gamma(c+m+\nu-\lambda+2r+3/2)}{\Gamma(r+1) \Gamma(\nu+r+1) (p/q)^{c+\nu+2\nu-\lambda+k-1}} \\ &\times \frac{1}{\Gamma(m-k+\frac{1}{2})} \cdot \int_0^1 x^{m-k-\frac{1}{2}} \cdot (1-x)^{(c+\nu-\lambda-m+2r+\frac{1}{2})} \\ &\times \left\{ 1 - \left( 1 - \frac{p}{q} \right) x \right\}^{-(k-m+\frac{1}{2})} dx; \end{aligned}$$

by virtue of the relation

$${}_2F_1[a, \beta; \gamma; x] = (1-x)^{\gamma-a-\beta} {}_2F_1[\gamma-a, \gamma-\beta; \gamma; x]$$

and (Baily, 1935)

$$F[a, b; c; z] = \frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)} \cdot \int_0^1 t^{b-1} (1-t)^{c-b-1} \cdot (1-zt)^{-a} dt$$

which reduces to

$$L_\lambda^\mu(t) = k_1 t^\nu \int_0^1 x^{m-\lambda-\frac{1}{2}} (1-x)^{c+\nu-\lambda-m+2r+\frac{1}{2}} \left\{ 1 - \left( 1 - \frac{p}{q} \right) x \right\}^{-(\lambda-m+\frac{1}{2})} \\ \times {}_2F_1 \left[ \begin{matrix} \frac{c}{2} + \frac{\nu}{2} + \frac{m}{2} - \frac{\lambda}{2} + \frac{3}{4}, \frac{c}{2} + \frac{\nu}{2} + \frac{m}{2} - \frac{\lambda}{2} + \frac{5}{4} \\ \nu + 1 \end{matrix} ; \frac{4q^2}{p^2} t^2 (1-x^2) \right] \frac{x}{p}$$

where  $k_1$  is a constant independent of  $x$ .

It follows by the definition of  $L_\lambda^\mu(t)$  that

$$L_\lambda^\mu(t) = 0(t^\nu)$$

for small values of  $t$ , and from the asymptotic expansion of  ${}_2F_1$ , we have

$$L_\lambda^\mu(t) = 0(t^{\lambda+\mu-3/2})$$

for large values of  $t$ .

3. *Corollary*—If we put  $q = 2$ ,  $c = \frac{1}{4}$ ,  $a = 1$ ,  $p = 1$ , and  $s = p$  in (A) we get

$$f(p^\mu) = \frac{p^\mu (\lambda - \frac{1}{2})}{2^{-\lambda+3/2}} \cdot \int_0^\infty y^{\lambda+\frac{1}{2}} \phi(y) \left( \frac{y}{4p} \right)^\nu \\ \times \sum_{r=0}^\infty \frac{(-1)^r \Gamma(\nu-\lambda+m+2r+7/4) \Gamma(\nu-\lambda-m+2r+7/4)}{r! \Gamma(\nu+r+1) \Gamma(\nu-\lambda-k+2r+9/4)} \left( \frac{1}{4} \cdot \frac{y}{p^\mu} \right)^{2r} \\ \times {}_2F_1 \left[ \begin{matrix} \nu - \lambda + m + 2r + 7/4, \nu - m - \lambda + 2r + 7/4 \\ \nu - \lambda - k + 2r + 9/4 \end{matrix} ; \frac{1}{2} \right], \quad (3.1)$$

The Laplace Stieltjes transform reduces to Whittaker transform. The above result was obtained by Bose, S. K.

## 4. Particular Cases—

CASE 1.— Let  $\mu = 1$ , then

$$\begin{aligned}
 f(s) &= s^{a-\nu+\lambda-3/2} q^{\lambda-\nu-3/2} \cdot \int_0^\infty \sum_{r=0}^\infty \frac{(-1)^r \left(\frac{1}{2}\right)^{\nu+2r} y^{\lambda+\nu+2r+\frac{1}{2}}}{\angle r \Gamma(\nu+r+1) s^{2r} q^{2r}} \phi(y) \\
 &\times \frac{\Gamma(c+m+\nu-\lambda+2r+3/2) \Gamma(c-m+\nu-\lambda+2r+3/2)}{\Gamma(c+\nu-\lambda+2r-k+2)} \\
 &\times {}_2F_1 \left[ \begin{matrix} c+m+\nu-\lambda+2r+3/2, (c-m+\nu-\lambda+2r+3/2 \\ c+\nu-\lambda+2r-k+2 \end{matrix} ; 1-p/q \right] dy,
 \end{aligned} \tag{4.1}$$

where  $R(c \pm m + \nu - \lambda + 3/2) > 0$ ,  $R(\nu + \alpha + \lambda + 3/2) > 0$ ,

$$R(c \pm m + \alpha + 1) > 0, R(ps) > 0.$$

If in this we put  $q = 1$  and  $p = 1$ , we get

$$\begin{aligned}
 f(s) &= s^{a-\nu+\lambda-3/2} \int_0^\infty \frac{(-1)^r \left(\frac{1}{2}\right)^{\nu+2r} y^{\lambda+\nu+2r+\frac{1}{2}}}{\angle r \Gamma(\nu+r+1) s^{2r}} \phi(y) \\
 &\times \frac{\Gamma(c+m+\nu-\lambda+2r+3/2) \Gamma(c-m+\nu-\lambda+2r+3/2)}{\Gamma(c+\nu-\lambda+2r-k+2)} dy,
 \end{aligned} \tag{4.2}$$

By the use of duplication formula

$$\Gamma(x+2r) = 2^{2r} \Gamma(x)_r \left(\frac{1}{2}x\right)_r \left(\frac{1}{2}x + \frac{1}{2}\right)_r,$$

(4.2) can be put as

$$\begin{aligned}
 &s^{a+\lambda-\nu+3/2} \cdot \int_0^\infty \frac{y^{\lambda+\nu+\frac{1}{2}}}{2^r} \Gamma \frac{(c+m+\nu-\lambda+3/2) \Gamma(c-m+\nu-\lambda+3/2)}{\Gamma(\nu+1) \Gamma(c+\nu-k-\lambda+2)} \\
 &{}_4F_3 \left\{ \begin{matrix} \frac{c}{2} + \frac{m}{2} + \frac{\nu}{2} - \frac{\lambda}{2} + \frac{3}{4}, \frac{c}{2} + \frac{m}{2} + \frac{\nu}{2} - \frac{\lambda}{2} + \frac{5}{4}, \frac{c}{2} - \frac{m}{2} + \frac{\nu}{2} - \frac{\lambda}{2} + \frac{3}{4}, \\ \frac{c}{2} - \frac{m}{2} + \frac{\nu}{2} - \frac{\lambda}{2} + \frac{5}{4}; \\ \nu+1, \frac{c}{2} + \frac{\nu}{2} - \frac{\lambda}{2} - \frac{k}{2} + 1, \frac{c}{2} + \frac{\nu}{2} - \frac{\lambda}{2} - \frac{k}{2} + \frac{3}{2} ; -\frac{y^2}{s^2} \end{matrix} \right\} \\
 &\times \phi(y) dy,
 \end{aligned} \tag{4.3}$$

where  $R(a + \nu + \lambda + 3/2) > 0$ ,  $R(c \pm m + \alpha + 1) > 0$ ,

$$R(c \pm m + \nu - \lambda + 3/2) > 0, R(s) > 0.$$

If in (4.1) we put  $q = 2$ ,  $c = \frac{1}{2}$ ,  $a = 1$ ,  $p = 1$  and  $\lambda = 0$ , we get the result of Tewari (1945).

CASE 2.—If we put  $\lambda = 0$ ,  $a = 0$  and  $c = m$  in (4.3) we find that  $\phi(t)$  is  $R_\nu$  and  $f(s)$  is the generalised Laplace transform of  $\phi(t)$ , then

$$f(s) = \frac{s^{-\nu-3/2} \Gamma(2m + \nu + 3/2) \Gamma(\nu + 3/2)}{2^\nu \Gamma(\nu + 1) \Gamma(m - k + \nu + 2)} \int_0^\infty y^{\nu+1/2} \phi(y) \\ \times {}_4F_3 \left[ \begin{matrix} m + \frac{\nu}{2} + \frac{3}{4}, m + \frac{\nu}{2} + \frac{5}{4}, \frac{\nu}{2} + \frac{3}{4}, \frac{\nu}{2} + \frac{5}{4} \\ \frac{m}{2} + \frac{\nu}{2} - \frac{k}{2} + 1, \frac{m}{2} + \frac{\nu}{2} - \frac{k}{2} + \frac{3}{2}, \nu + 1 \end{matrix} ; -\frac{y^2}{s^2} \right] dy, \quad (4.4)$$

where  $R(a + \nu + 3/2) > 0$ ,  $R(m \pm m + \alpha + 1) > 0$ ,

$$R(m \pm m + \nu + 3/2) > 0, R(s) > 0.$$

Corresponding results for ordinary Laplace transform can be obtained by putting  $k = \frac{1}{2} - m$  in (4.4).

CASE 3.—If we put  $\lambda = 0$  in (4.1), we get:—

If  $\phi(t)$  is  $R_\nu$  and  $f(s)$  is the generalised Laplace transform of  $\phi(t)$  in the form given by Saksena, then,

$$f(s) = s^{\alpha-\nu-3/2} q^{-\nu-3/2} \int_0^\infty \sum_{r=0}^\infty \frac{(-1)^r (\frac{1}{2})^{\nu+2r} y^{\nu+2r+1/2}}{\Gamma(\nu + r + 1) \cdot \mathcal{L}r s^{2r} q^{2r}} \phi(y) \\ \times \frac{\Gamma(c + m + \nu + 2r + 3/2) \Gamma(c - m + \nu + 3/2 + 2r)}{\Gamma(c + \nu + 2r - k + 2)} \\ \times {}_2F_1 \left[ \begin{matrix} c + m + \nu + 2r + 3/2, c - m + \nu + 2r + 3/2 \\ c + \nu + 2r - k + 2 \end{matrix} ; 1 - p/q \right] dy, \quad (4.5)$$

where  $R(c \pm m + \nu + 3/2) > 0$ ,  $R(\nu + \alpha + \lambda + 3/2) > 0$ ,

$$R(c \pm m + \nu - \lambda + 3/2) > 0, R(s) > 0.$$

CASE 4.—Let  $\mu = \frac{1}{2}$ , then

$$\begin{aligned} f(\sqrt{s}) &= s^{\frac{1}{2}(\alpha-\nu+\lambda-3/2)} q^{\lambda-\nu-3/2} \int_0^\infty \sum_{r=0}^\infty \frac{(-1)^r \left(\frac{1}{2}\right)^{\nu+2r} y^{\lambda+\nu+2r+\frac{1}{2}}}{\mathcal{L}r \Gamma(\nu+r+1) s^r q^{2r}} \phi(y) \\ &\times \frac{\Gamma(c+m+\nu-\lambda+2r+3/2) \Gamma(c-m+\nu-\lambda+2r+3/2)}{\Gamma(c+\nu-\lambda+2r-k+2)} \\ &\times {}_2F_1 \left[ \begin{matrix} c+m+\nu-\lambda+2r+3/2, (c-m+\nu-\lambda+2r+3/2) \\ c+\nu-\lambda+2r-k+2 \end{matrix} ; 1-p/q \right] dy, \end{aligned} \quad (4.6)$$

where  $R(c \pm m + \nu - \lambda + 3/2) > 0$ ,  $R(\nu + \alpha + \lambda + 3/2) > 0$ ,

$$R(c \pm m + \alpha + 1) > 0, R(ps^{\frac{1}{2}}) > 0.$$

If in (4.6) we put  $q = 2$ ,  $c = \frac{1}{4}$ ,  $\alpha = 1$ ,  $p = 1$ ,  $k = \frac{1}{4}$ , and  $m = \pm \frac{1}{4}$ , we get

$$\begin{aligned} f(\sqrt{s}) &= \frac{1}{(\sqrt{s})^{-\lambda+\frac{1}{2}}} \int_0^\infty y^{\lambda+\frac{1}{2}} \phi(y) \left( \frac{y}{2\sqrt{s}} \right)^\nu \sum_{r=0}^\infty \frac{(-1)^r \Gamma(\nu-\lambda+2r+3/2)}{\mathcal{L}r \Gamma(1+\nu+r)} \\ &\times \left( \frac{y}{2\sqrt{s}} \right)^{2r} \cdot dy \end{aligned} \quad (4.7)$$

On using

$$\frac{1}{p^n} = \frac{x^n}{\Gamma(n+1)}$$

and

$$z^{m+\frac{1}{2}} \cdot e^{\frac{1}{2}z} {}_1F_1 \left[ \begin{matrix} \frac{1}{2} + m + k \\ 1 + 2m \end{matrix} ; -z \right] = M_{k,m}(z),$$

we get a result of Gupta (1945).

*Example.*—Setting  $\phi(t) = e^{-\frac{1}{2}t^2}$

and using the result (4.3) with  $\lambda = \nu + \frac{1}{2}$ , we find, since

$$t^{\nu+\frac{1}{2}} e^{-\frac{1}{2}t^2}$$

is  $R_\nu$ , that

$$s^{\alpha-1} \int_0^\infty \frac{1}{2^\nu} y^{2\nu+1} \frac{\Gamma(c+m+1) \Gamma(c-m+1)}{\Gamma(\nu+1) \Gamma(c-k+3/2)} \cdot e^{-\frac{1}{2}y^2} dy$$

$$\times {}_4F_3 \left[ \begin{matrix} \frac{c}{2} + \frac{m}{2} + \frac{1}{2}, \frac{c}{2} + \frac{m}{2} + 1, \frac{c}{2} - \frac{m}{2} + \frac{1}{2}, \frac{c}{2} - \frac{m}{2} + 1 \\ \nu + 1, \frac{c}{2} - \frac{k}{2} + \frac{3}{4}, \frac{c}{2} - \frac{k}{2} + \frac{5}{4} \end{matrix} ; -\frac{y^2}{s^2} \right] dy$$

$$= s^a \int_0^\infty (st)^{c-\frac{1}{2}} \cdot e^{-\frac{1}{2}st} W_{k,m}(st) e^{-\frac{1}{2}t^2} dt$$

An interesting particular case of the theorem is obtained by putting  $\lambda = 0$ ,  $\nu = \frac{1}{2}$  and  $\mu = 1$ .

If  $\phi(t)$  is  $R_r$

and  $f(s)$  is the generalised Laplace transform of  $\phi(t)$  in the form given by Saksena, then

$$f(s) = s^{a-2} q^{-2} \int_0^\infty \sum_{r=0}^\infty \frac{(-1)^r (\frac{1}{2})^{2r+\frac{1}{2}} y^{2r+1}}{\Gamma(r) \Gamma(r+3/2) \cdot s^{2r} q^{2r}} \phi(y)$$

$$\times \frac{\Gamma(c+m+2r+2) \Gamma(c-m+2r+2)}{\Gamma(c-k+2r+5/2)}$$

$$\times {}_2F_1 \left[ \begin{matrix} c+m+2r+2, c-m+2r+2 \\ c-k+2r+5/2 \end{matrix} ; 1-p/q \right] dy, \quad (4.8)$$

where  $R(c \pm m + 2) > 0$ ,  $R(a + 2) > 0$ .

Another interesting particular case of the theorem is obtained by putting  $\lambda = 0$ ,  $\nu = -\frac{1}{2}$  and  $\mu = 1$ . If

$\phi(t)$  is  $R_c$

and  $f(s)$  is the generalised Laplace transform of  $\phi(t)$  in the form given by Saksena, then

$$f(s) = \frac{s^{a-1}}{q} \int_0^\infty \sum_{r=0}^\infty \frac{(-1)^r (\frac{1}{2})^{2r-\frac{1}{2}} \cdot y^{2r}}{\Gamma(r) \Gamma(r+\frac{1}{2}) s^{2r} q^{2r}} \phi(y)$$

$$\times \frac{\Gamma(c+m+2r+1) \Gamma(c-m+2r+1)}{\Gamma(c+2r+3/2-k)}$$

$${}_2F_1 \left[ \begin{matrix} c+m+2r+1, c-m+2r+1 \\ c-k+2r+3/2 \end{matrix} ; 1-p/q \right] dy \quad (4.9)$$

where  $R(c \pm m + 1) > 0$ ,  $R(a + 1) > 0$ .



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# STUDY OF A GENERALISED LAPLACE TRANSFORM

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1. The Laplace-Stieltjes transform in the classical form is

$$f(s) = \int_0^{\infty} e^{-st} d\alpha(t), \quad (1.1)$$

where  $\alpha(t)$  is a function of bounded variation.

Generalisations of this integral have been given by Meijer<sup>1</sup>, Boas<sup>2</sup> and Varma.<sup>3</sup>

Recently (1949) Dr. Varma has given another generalisation of (1.1) in the form<sup>4</sup>

$$f(s) = \int_0^{\infty} (st)^{m-\frac{1}{2}} e^{-\frac{1}{2}st} W_{k,m}(st) d\alpha(t), \quad (1.2)$$

where  $\alpha(t)$  denotes a function of bounded variation in  $0 \leq t \leq R$  for every  $R$  and  $m \geq 0$ .

The kernel in this generalisation possesses the property

$$\frac{d}{dz} \left[ z^{m-\frac{1}{2}} e^{-\frac{1}{2}z} W_{k,m}(z) \right] = -z^{m-1} e^{-\frac{1}{2}z} W_{k+\frac{1}{2}, m-\frac{1}{2}}(z) \quad (1.3)$$

which is similar to  $\frac{d}{dz}(e^{-z}) = -e^{-z}$ .

If we put  $k + m = \frac{1}{2}$ , the integral (1.2) reduces to (1.1) as

$$(st)^{m-\frac{1}{2}} e^{-\frac{1}{2}st} W_{\frac{1}{2}-m,m}(st) = e^{-st}$$

As all absolutely continuous functions are necessarily of bounded variation we shall take  $\alpha(t)$  to be absolutely continuous and in that case (1.2)

$$\text{becomes } f(s) = \int_0^{\infty} (st)^{m-\frac{1}{2}} e^{-\frac{1}{2}st} W_{k,m}(st) \phi(t) dt, \quad (1.4)$$

where

$$da(t) = \phi(t) dt.$$

In this paper I have given the generalised Laplace transforms of certain functions and have also established a relation between the order property of  $a(t)$  and the convergence property of the generalised Laplace transform (1.2).

2. *Example 1.*—If  $\phi(t) = t^h T_l^n(t)$ ,

where  $T_l^n(t)$  is Sonine's polynomial defined by

$$T_l^n(t) = \frac{(-)^n}{\Gamma(n+1)\Gamma(l+1)} {}_1F_1(-n; l+1; t)$$

then

$$f(s) = \frac{1}{s^{h+1}} \cdot \frac{(-1)^n \Gamma(h+1) \Gamma(2m+h+1)}{\Gamma(l+1) \Gamma(n+1) \Gamma(m-k+h+3/2)} \\ \times {}_3F_2 \left[ \begin{matrix} h+1, 2m+h+1, -n \\ l+1, m-k+h+3/2 \end{matrix} ; \frac{1}{s} \right],$$

where

$$R(h+1) > 0, R(2m+h+1) > 0, |s| > 1, R(s) > 0.$$

*Example 2.*—If  $\phi(t) = He_n(t)$ ,

where  $He_n(t)$  is Hermite's polynomial defined by

$$He_n(t) = (-)^n e^{\frac{t^2}{2}} \frac{d^n}{dt^n} (e^{-\frac{t^2}{2}})$$

then

$$f(s) = \frac{\Gamma(2m+n+1) \Gamma(n+1)}{s^{n+1} \Gamma(m+n-k+3/2)} \\ \times {}_2F_2 \left( \begin{matrix} \frac{-m-n+k}{2} - \frac{1}{4}, \frac{-m-n+k}{2} + \frac{1}{4} \\ -m - \frac{n}{2}, -m - \frac{n}{2} + \frac{1}{2} \end{matrix} ; -\frac{s^2}{2} \right),$$

where

$$R(2m+1) > 0 \text{ when } n \text{ is even,}$$

$$R(m+1) > 0 \text{ when } n \text{ is odd,}$$

and

$$R(s) > 0.$$

Example 3.—If

$$\phi(t) = t^{l-1} {}_pF_q(a_1, a_2, \dots, a_p; \beta_1, \beta_2, \dots, \beta_q; t)$$

then using the following result, due to Sinha,<sup>5</sup>

$$\begin{aligned} & \int_0^\infty u^{l-1} e^{-cu} W_{k,m}(u) {}_pF_q(a_1, a_2, \dots, a_p; \beta_1, \beta_2, \dots, \beta_q; cu) du \\ &= \frac{\Gamma(l+m+\frac{1}{2}) \Gamma(l-m+\frac{1}{2})}{\Gamma(l-k+1)} \\ & \times {}_{p+2}F_{q+1} \left[ \begin{matrix} a_1, a_2, \dots, a_p, l+m+\frac{1}{2}, l-m+\frac{1}{2} \\ \beta_1, \beta_2, \dots, \beta_q, l-k+1 \end{matrix}; c \right], \end{aligned}$$

where

$$R(l \pm m + \frac{1}{2}) > 0, p+1 \leq q$$

and also  $|c| < 1$ , when  $p = q$ ,

we have

$$\begin{aligned} f(s) &= \frac{1}{s^l} \cdot \frac{\Gamma(l+2m) \Gamma(l)}{\Gamma(l+m-k+\frac{1}{2})} \\ & \times {}_{p+2}F_{q+1} \left[ \begin{matrix} a_1, a_2, \dots, a_p, l+2m, l \\ \beta_1, \beta_2, \dots, \beta_q, l-k+m+\frac{1}{2} \end{matrix}; \frac{1}{s} \right], \end{aligned}$$

where

$$R(l+2m) > 0, R(l) > 0, p+1 \leq q \text{ and } R(s) > 0.$$

If  $p = q$ , we must also have  $|s| > 1$ .

Putting  $p = 2, q = 3$  and using the result<sup>6</sup>

$$\begin{aligned} {}_2F_3 \left( a, \rho - a; \rho, \frac{1}{2}\rho, \frac{1}{2}\rho + \frac{1}{2}; \frac{x^2}{4} \right) &= {}_1F_1(a; \rho; x) \\ {}_1F_1(a; \rho; -x) \end{aligned}$$

we find that the generalised Laplace transform of

$$t^{l-1} {}_1F_1(a; \rho; 2\sqrt{t}) \cdot {}_1F_1(a; \rho; -2\sqrt{t})$$

is

$$\begin{aligned} f(s) &= \frac{1}{s^l} \cdot \frac{\Gamma(l+2m) \Gamma(l)}{\Gamma(l+m-k+\frac{1}{2})} \\ & \times {}_4F_4 \left\{ \begin{matrix} a, \rho - a, l+2m, l \\ \rho, \frac{1}{2}\rho, \frac{1}{2}\rho + \frac{1}{2}, l-k+m+\frac{1}{2} \end{matrix}; \frac{1}{s} \right\}, \end{aligned}$$

where

$$R(s) > 0, R(l + 2m) > 0, R(l) > 0.$$

*Example 4.*—If  $\phi(t) = P_n^{(\alpha, \beta)}(t)$ , where  $P_n^{(\alpha, \beta)}(t)$  denotes Jacobi's polynomial defined by

$$\begin{aligned} P_n^{(\alpha, \beta)}(t) &= \binom{n + \alpha}{n} {}_2F_1(-n, n + \alpha + \beta + 1; \alpha + 1; \frac{1-t}{2}) \\ &= \frac{1}{|n|} \sum_{\nu=0}^n \binom{n}{\nu} (n + \alpha + \beta + 1)_\nu (\alpha + \nu + 1)_{n-\nu} \left(\frac{t-1}{2}\right)^\nu. \end{aligned}$$

then

$$\begin{aligned} f(s) &= \frac{1}{s} \cdot \frac{1}{|n|} \cdot \sum_{\nu=0}^n \frac{1}{2^\nu} \cdot \frac{1}{s^\nu} \binom{n}{\nu} (n + \alpha + \beta + 1)_\nu (\alpha + \nu + 1)_{n-\nu} \\ &\quad \times \frac{\Gamma(2m + \nu + 1) \Gamma(\nu + 1)}{\Gamma(m - k + \nu + 3/2)} \\ &\quad \times {}_2F_1 \left[ \begin{matrix} -n + \nu, n + \alpha + \beta + \nu + 1 \\ \alpha + \nu + 1 \end{matrix}; \frac{1}{2} \right], \end{aligned}$$

where

$$R(2m + 1) > 0, R(s) > 0.$$

As a particular case of this we find that the generalised Laplace transform of the ultraspherical polynomial  $P_n^{(\lambda)}(t)$  defined by<sup>7</sup>

$$P_n^{(\lambda)}(t) = \frac{\Gamma(\lambda + \frac{1}{2}) \Gamma(n + 2\lambda)}{\Gamma(2\lambda) \Gamma(n + \lambda + \frac{1}{2})} P_n^{(\lambda - \frac{1}{2}, \lambda - \frac{1}{2})}(t)$$

is given by

$$\begin{aligned} f(s) &= \frac{\Gamma(\lambda + \frac{1}{2})}{\Gamma(2\lambda) \Gamma(n + \lambda + \frac{1}{2})} \cdot \frac{1}{s} \cdot \frac{1}{|n|} \sum_{\nu=0}^n \frac{1}{2^\nu s^\nu} \binom{n}{\nu} (\lambda + \nu + \frac{1}{2})_{n-\nu} \\ &\quad \times \frac{\Gamma(n + 2\lambda + \nu) \Gamma(2m + \nu + 1) \Gamma(\nu + 1)}{\Gamma(m - k + \nu + 3/2)} \\ &\quad \times {}_2F_1 \left[ \begin{matrix} -n + \nu, n + 2\lambda + \nu \\ \lambda + \nu + \frac{1}{2} \end{matrix}; \frac{1}{2} \right], \end{aligned}$$

$$R(2m + 1) > 0, R(s) > 0,$$

which reduces to

$$\frac{\Gamma(\lambda + \frac{1}{2}) \Gamma(\frac{1}{2})}{\Gamma(2\lambda) \Gamma(n + \lambda + \frac{1}{2})} \cdot \frac{1}{s} \cdot \frac{1}{\angle n} \sum_{\nu=0}^n \frac{1}{2^\nu s^\nu} \binom{n}{\nu} (\lambda + \nu + \frac{1}{2})_{n-\nu} \\ \times \frac{\Gamma(n + 2\lambda + \nu) \Gamma(2m + \nu + 1) \Gamma(\nu + 1) \Gamma(\lambda + \nu + \frac{1}{2})}{\Gamma(m - k + \nu + \frac{3}{2}) \Gamma(-\frac{n}{2} + \frac{\nu}{2} + \frac{1}{2}) \Gamma(\frac{n + \nu}{2} + \lambda + \frac{1}{2})},$$

$$R(2m + 1) > 0, R(s) > 0$$

by using the result

$${}_2F_1 \left[ \begin{matrix} a, b \\ \frac{1}{2}(a + b + 1) \end{matrix} ; \frac{1}{2} \right] = \frac{\Gamma(\frac{1}{2}) \Gamma(\frac{1}{2} + \frac{1}{2}a + \frac{1}{2}b)}{\Gamma(\frac{1}{2} + \frac{1}{2}a) \Gamma(\frac{1}{2} + \frac{1}{2}b)}.$$

*Example 5.*—If  $\phi(t) = t^\mu e^{-at} J_n(\beta t)$ ,

where  $J_n(\beta t)$  is Bessel function, then

$$f(s) = \sum_{r=0}^{\infty} \frac{(\frac{1}{2}\beta)^{n+2r} (-1)^r \Gamma(n + 2m + \mu + 2r + 1) \Gamma(n + \mu + 2r + 1)}{s^{n+\mu+2r+1} \cdot \angle r \cdot \Gamma(n + r + 1) \Gamma(n + m - k + \mu + 2r + 3/2)} \\ \times {}_2F_1 \left[ \begin{matrix} n + 2m + \mu + 2r + 1, n + \mu + 2r + 1 \\ n + m - k + \mu + 2r + 3/2 \end{matrix} ; -\frac{a}{s} \right],$$

where

$$R(n + 2m + \mu + 1) > 0, R(n + \mu + 1) > 0, R(s + a) > 0,$$

$$|s + a| > |\beta|.$$

*Example 6.*—If  $\phi(t) = J_\mu(2a\sqrt{t}) J_\nu(2b\sqrt{t})$

then

$$f(s) = \sum_{r=0}^{\infty} \frac{(-1)^r a^{\mu+2r} b^\nu}{\angle r \Gamma(\nu + 1) s^{\frac{\mu+\nu}{2} + r + 1}} \cdot \frac{\Gamma(\frac{\mu + \nu}{2} + r + 1)}{\Gamma(\mu + r + 1)} \\ \times \frac{\Gamma(\frac{\mu + \nu}{2} + 2m + r + 1)}{\Gamma(\frac{\mu + \nu}{2} + m - k + r + \frac{3}{2})} {}_2F_1 \left( -r, -\mu - r; \nu + 1; \frac{b^2}{a^2} \right),$$

where

$$R\left(\frac{\mu + \nu}{2} + 1\right) > 0, R\left(\frac{\mu + \nu}{2} + 2m + 1\right) > 0, R(s) > 0,$$

To establish the result we use the expansion<sup>8</sup>

$$J_{\mu}(az) J_{\nu}(bz) = \frac{(\frac{1}{2}az)^{\mu} (\frac{1}{2}bz)^{\nu}}{\Gamma(\nu+1)} \sum_{r=0}^{\infty} \frac{(-)^m (\frac{1}{2}az)^{2m} \cdot {}_2F_1\left(-m, -\mu-m; \nu+1; \frac{b^2}{a^2}\right)}{m! \Gamma(\mu+m+1)}$$

true for all values of  $\mu$  and  $\nu$  and integrate term by term with the help of Goldstein's formula<sup>9</sup> which is justifiable.

Putting  $b = a$  and using the result<sup>10</sup>

$${}_2F_1(a, b; c; 1) = \frac{\Gamma(c) \Gamma(c-a-b)}{\Gamma(c-a) \Gamma(c-b)}$$

and the duplication formula

$$\Gamma(x+2r) = 2^{2r} \Gamma(x) \left(\frac{1}{2}x\right)_r \left(\frac{1}{2}x + \frac{1}{2}\right)_r$$

we find that the generalised Laplace transform of  $J_{\mu}(2a\sqrt{t}) J_{\nu}(2a\sqrt{t})$  is

$$f(s) = \frac{a^{\mu+\nu}}{s^{\frac{\mu+\nu}{2}+1}} \cdot \frac{\Gamma\left(\frac{\mu+\nu}{2}+1\right) \Gamma\left(\frac{\mu+\nu}{2}+2m+1\right)}{\Gamma(\mu+1) \Gamma(\nu+1) \Gamma\left(\frac{\mu+\nu}{2}+m-k+\frac{3}{2}\right)} \\ \times {}_4F_4\left[\begin{matrix} \frac{\mu+\nu}{2}+1, \frac{\mu+\nu}{2}+1, \frac{\mu+\nu}{2}+2m+1, \frac{\mu+\nu+1}{2} \\ \mu+1, \nu+1, \mu+\nu+1, \frac{\mu+\nu}{2}+m-k+\frac{3}{2} \end{matrix}; -\frac{4a^2}{s}\right],$$

where

$$R\left(\frac{\mu+\nu}{2}+1\right) > 0, R\left(\frac{\mu+\nu}{2}+2m+1\right) > 0, R(s) > 0.$$

If we put  $b = ia$  and  $\mu = \nu$  and use Kummer's formula

$${}_2F_1(\alpha, \beta; \alpha-\beta+1; -1) = \frac{\Gamma(\alpha-\beta+1) \Gamma(\frac{1}{2})}{2^{\alpha} \Gamma(\frac{1}{2}\alpha+\frac{1}{2}) \Gamma(\frac{1}{2}\alpha-\beta+1)}$$

we find that the generalised Laplace transform of  $J_{\nu}(2a\sqrt{t}) I_{\nu}(2a\sqrt{t})$  is

$$f(s) = \frac{a^{2\nu} \Gamma(\nu+2m+1)}{s^{\nu+1} \Gamma(\nu+1) \Gamma(\nu+m-k+3/2)} \\ \times {}_2F_3\left[\begin{matrix} \nu+m+\frac{1}{2}, \nu+m+1 \\ \frac{\nu}{2}+m+1, \frac{\nu}{2}+\frac{m}{2}-\frac{k}{2}+\frac{3}{4} \end{matrix}; -\frac{a^4}{s^2}\right],$$

where

$$R(\nu + 1) > 0, R(\nu + 2m + 1) > 0, R(s) > 0.$$

3. I now give the theorem establishing the relation between the order property of  $\alpha(t)$  and the convergence property of the generalised Laplace transform.

*Theorem.*—If  $\alpha(t) = O(e^{\gamma t}) \quad (t \rightarrow \infty)$

for some real number  $\gamma$ , then the integral (1.2) converges for  $\sigma > \gamma$ .

For, integrating by parts, we have

$$\begin{aligned} & \int_0^R (st)^{m-\frac{1}{2}} e^{-\frac{1}{2}st} W_{k,m}(st) d\alpha(t) \\ &= [\alpha(R) \cdot (sR)^{m-\frac{1}{2}} e^{-\frac{1}{2}sR} \cdot W_{k,m}(sR)] \\ &+ s \int_0^R (st)^{m-1} e^{-\frac{1}{2}st} W_{k+\frac{1}{2}, m-\frac{1}{2}}(st) \alpha(t) dt \end{aligned}$$

using the property (1.3).

Now  $W_{k,m}(x) = O(x^k e^{-\frac{1}{2}x})$  when  $x$  is large.

Therefore

$$\alpha(R) (sR)^{m-\frac{1}{2}} e^{-\frac{1}{2}sR} W_{k,m}(sR) = o(1) \quad (R \rightarrow \infty, \sigma > \gamma).$$

Since  $\alpha(t)$  is assumed to be of bounded variation in every finite interval our hypothesis implies that

$$|\alpha(t)| \leq M e^{\gamma t} \quad (0 \leq t < \infty)$$

where  $M$  is a constant.

Hence

$$\begin{aligned} & \int_0^\infty (st)^{m-1} e^{-\frac{1}{2}st} W_{k+\frac{1}{2}, m-\frac{1}{2}}(st) \alpha(t) dt \\ & \leq \frac{M}{|s|} \int_0^\infty (st)^{m-1} e^{-(\frac{\sigma}{2} + \frac{1}{2})st} W_{k+\frac{1}{2}, m-\frac{1}{2}}(st) d(st) \\ & \leq \frac{M}{|s|} \cdot \frac{\Gamma(2m)}{\Gamma(m-k+\frac{1}{2})} \cdot {}_2F_1 \left[ \begin{matrix} 2m, 1 \\ m-k+\frac{1}{2} \end{matrix}; \frac{\gamma}{s} \right] \end{aligned}$$

integrating the right-hand side with the help of Goldstein's formula.



The right-hand side is a convergent series if  $\gamma < R(s) < \sigma$  and so the integral on the left-hand side of the inequality converges absolutely for  $\sigma > \gamma$ .

But

$$\begin{aligned} & \int_0^{\infty} (st)^{m-\frac{1}{2}} e^{-\frac{1}{2}st} W_{k,m}(st) da(t) \\ &= s \int_0^{\infty} (st)^{m-1} e^{-\frac{1}{2}st} W_{k+\frac{1}{2}, m-\frac{1}{2}}(st) a(t) dt. \end{aligned}$$

Hence our theorem is established.

*Corollary.*—If  $\alpha(\infty)$  exists and if

$$a(t) - \alpha(\infty) = O(e^{\gamma t}) \quad (t \rightarrow \infty)$$

for some real number  $\gamma$ , then the integral (1.2) converges for  $\sigma > \gamma$ .

This follows immediately since

$$\begin{aligned} & \int_0^{\infty} (st)^{m-\frac{1}{2}} e^{-\frac{1}{2}st} W_{k,m}(st) d[a(t) - \alpha(\infty)] \\ &= \int_0^{\infty} (st)^{m-\frac{1}{2}} e^{-\frac{1}{2}st} W_{k,m}(st) da(t). \end{aligned}$$

I am indebted to Dr. R. S. Varma for guidance and help in the preparation of this paper.

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# A THEOREM FOR THE GENERALISED LAPLACE TRANSFORM

By S. P. KAUSHIK, *Bikaner*

(Communicated by Dr. R. S. Varma)

Tricomi<sup>1</sup> in 1935 gave the Hankle transform of the function  $x^{-\frac{1}{2}\nu} f(x)$  when

$$F(p) \doteq \int_0^\infty f(x) dx$$

i.e.,

$$F(p) = p \int_0^\infty e^{-px} f(x) dx$$

in the form,

$$p^{-\nu+1} F\left(\frac{1}{p}\right) \doteq \int_0^\infty \left(\frac{x}{s}\right)^{\frac{1}{2}\nu} J_\nu(2\sqrt{xs}) f(s) ds.$$

It is possible to generalise this result when  $F(p)$  is a Whittaker transform of  $f(x)$  in the sense of Varma, i.e.,

when

$$F(p) = p \int_0^\infty (2xp)^{-\frac{1}{2}} W_{k,m}(2xp) f(x) dx. \quad (1)$$

To obtain such a generalisation, we note<sup>2</sup> that,

$$W_{k,m}(z) = \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2} - m - k)} M_{k,m}(z) + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2} + m - k)} M_{k,-m}(z) \quad (2)$$

where

$$M_{k,m}(z) = e^{-\frac{1}{2}z} z^{\frac{1}{2}+m} \sum_{r=0}^{\infty} \frac{(\frac{1}{2} + m - k, r)}{r! (1 + 2m, r)} z^r$$

and

$$M_{k,-m}(z) = e^{-\frac{1}{2}z} \cdot z^{\frac{1}{2}-m} \sum_{r=0}^{\infty} \frac{(\frac{1}{2} - m - k, r)}{r! (1 - 2m, r)} z^r.$$

Substituting the value of  $W_{k,m}(z)$  in (1)

1. Tricomi, *Rend. Acc. dei Lincei*, 22, 564.

2. Whittaker & Watson, *Modern Analysis*, University Press, Cambridge, 1935, p. 346.

we have

$$\begin{aligned}
 p^{1-\nu} F\left(\frac{1}{p}\right) &= p^{-\nu} \int_0^\infty \left(\frac{2s}{p}\right)^{-\frac{1}{2}} \left[ \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-m-k)} \left(\frac{2s}{p}\right)^{\frac{1}{2}+m} e^{-\frac{s}{p}} \right. \\
 &\quad \times \sum_{r=0}^\infty \frac{(\frac{1}{2}+m-k, r)}{r!(1+2m, r)} \left(\frac{2s}{p}\right)^r + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}+m-k)} \left(\frac{2s}{p}\right)^{\frac{1}{2}-m} e^{-\frac{s}{p}} \\
 &\quad \left. \times \sum_{r=0}^\infty \frac{(\frac{1}{2}-m-k, r)}{r!(1-2m, r)} \left(\frac{2s}{p}\right)^r \right] f(s) ds. \quad (3)
 \end{aligned}$$

Now suppose that

$$\frac{1}{p} \doteq x$$

We interpret each term of the above by the help of  $\left(\frac{y}{p}\right)^{\frac{1}{2}} e^{-\frac{y}{p}} \doteq (xy)^{\frac{1}{2}}$   $J_1(2\sqrt{xy})$  a result of *Pol*,<sup>3</sup> and we get that

$$\begin{aligned}
 p^{1-\nu} \phi_m \left(\frac{1}{p}\right) &\doteq \int_0^\infty \left[ \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-m-k)} \frac{2^{m+\frac{1}{2}}}{s^\nu} \sum_{r=0}^\infty \frac{(\frac{1}{2}+m-k, r)}{r!(1+2m, r)} 2^r \right. \\
 &\quad \times (xs)^{\frac{1}{2}(\nu+m+r+\frac{1}{4})} J_{\nu+m+r+\frac{1}{4}}(2\sqrt{xs}) + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}+m-k)} \frac{2^{\frac{1}{2}-m}}{s^\nu} \\
 &\quad \left. \times \sum_{r=0}^\infty \frac{(\frac{1}{2}-m-k, r)}{r!(1-2m, r)} 2^r (xs)^{\frac{1}{2}(\nu-m+r+\frac{1}{4})} J_{\nu-m+r+\frac{1}{4}}(2\sqrt{xs}) \right] \\
 &\quad \times f(s) ds. \quad (4)
 \end{aligned}$$

When  $k = \frac{1}{4}$ ,  $m = -\frac{1}{4}$ , the second series reduces to zero, only the first term of the first series survives and we get Tricomi's result.

As an example let us take,

$$f(x) \equiv e^{-x},$$

3. P. Humbert, *le calcul Symbolique* (Hermann & Co., Paris), 1934, p. 30.

Since<sup>4</sup>

$$\begin{aligned} \int_0^\infty J_\nu(at) e^{-p^2 t^2} t^{\mu-1} dt \\ = \frac{\Gamma(\frac{1}{2}\mu + \frac{1}{2}\nu) a^\nu}{\Gamma(\nu+1) 2^{\nu+1} p^{\mu+\nu}} {}_1F_1 \left[ \frac{\mu+\nu}{2}, \nu+1; -\frac{a^2}{4p^2} \right] \\ |arg(p)| < \frac{\pi}{4}; R(\mu+\nu) > 0. \end{aligned}$$

The right-hand side of (4) reduces to

$$\begin{aligned} \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-m-k)} 2^{m+1} \sum_{r=0}^\infty \frac{(\frac{1}{2}+m-k, r)}{r!(1+2m, r)} 2^r s^{m+r+\frac{1}{2}} e^{-s} \\ + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}+m-k)} 2^{-m+1} \sum_{r=0}^\infty \frac{(\frac{1}{2}-m-k, r)}{r!(1-2m, r)} 2^r s^{-m+r+\frac{1}{2}} e^{-s} \\ = e^{-s} (2s)^{-\frac{1}{2}} \left[ \frac{\Gamma(-2m)}{\Gamma(\frac{1}{2}-m-k)} (2s)^{\frac{1}{2}+m} \sum_{r=0}^\infty \frac{(\frac{1}{2}+m-k, r)}{r!(1+2m, r)} (2s)^r \right. \\ \left. + \frac{\Gamma(2m)}{\Gamma(\frac{1}{2}+m-k)} (2s)^{\frac{1}{2}-m} \sum_{r=0}^\infty \frac{(\frac{1}{2}-m-k, r)}{r!(1-2m, r)} (2s)^r \right] \\ = (2s)^{-\frac{1}{2}} W_{k,m}(2s). \end{aligned}$$

From (I) we have by using Goldstein's formula,<sup>5</sup>

$$\phi_m^k(p) = \frac{\Gamma(m+\frac{5}{4}) \Gamma(\frac{5}{4}-m)}{2 \Gamma(\frac{7}{4}-k)} {}_2F_1 \left[ \begin{matrix} \frac{5}{4}+m, \frac{5}{4}-m \\ \frac{7}{4}-k \end{matrix}; \frac{1}{2} - \frac{1}{2p} \right].$$

Therefore,

$$\begin{aligned} p^{1-\nu} \phi_m^k \left( \frac{1}{p} \right) &= \frac{p^{1-\nu}}{2} \frac{\Gamma(m+\frac{5}{4}) \Gamma(\frac{5}{4}-m)}{\Gamma(\frac{7}{4}-k)} \\ &\quad {}_2F_1 \times \left[ \begin{matrix} m+\frac{5}{4}, -m+\frac{5}{4} \\ \frac{7}{4}-k \end{matrix}; \frac{1}{2} - \frac{p}{2} \right]. \end{aligned}$$

4. Copson, *Complex variable* (Oxford University Press), p. 342.

5. Goldstein, *Proc. Lond. Math. Soc.*, 34 (1932), pp. 103-25.

Hence, by our theorem,

$$\frac{p^{1-p}}{2} \frac{\Gamma\left(m + \frac{5}{4}\right) \Gamma\left(\frac{5}{4} - m\right)}{\Gamma\left(\frac{7}{4} - k\right)} {}_2F_1\left[\begin{matrix} m + \frac{5}{4}, \frac{5}{4} - m \\ \frac{7}{4} - k \end{matrix}; \frac{1}{2} - \frac{p}{2}\right] \\ \doteq (2s)^{-\frac{1}{2}} W_{k,m}(2s) \\ -1 < R(p) < 3, R\left(\pm m + \frac{5}{4}\right) > 0.$$

This is substantially equal to a known\* result.

I take this opportunity to thank Dr. R. S. Varma for suggestion and help.

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\* Mc Lachlan and Humbert, *Formulaire pour le calcul Symbolique* (Gauthier-Villars, Paris), 1941, p. 61.

# ON EXCEPTIONAL VALUES OF MEROMORPHIC FUNCTIONS—I

(A NOTE)

BY YOGENDRA BEHARI LAL MATHUR

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(Communicated by Dr. P. L. Srivastava)

1. The exceptional values of meromorphic functions have been made a topic of study from two points of view. We may study an entire category of exceptional values, *e.g.*, a set of deficient values, or alternatively, we may choose an individual particular value and study its properties.

2. E. F. Collingwood, in an interesting paper, has studied the individual exceptional values. Theorems of a restricted nature and having a bearing on this problem have been known since the inception of the theory of Nevanlinna.

3. In accordance with Collingwood, we study a function  $f(z)$ , which is meromorphic and not rational in the domain

$$|z| < R \leq \infty.$$

Let  $a$  be any complex number, infinity not excluded. A zero of  $f(z) - a$ , when  $a \neq 0$ , or a pole of  $f(z)$  when  $a = \infty$  will be called an  $a$ -point of  $f(z)$ . In the standard notation of Nevanlinna's "Theoreme de Picard-Borel et la Theorie des Fonctions Meromorphes (1929)" and "Eindeutige Analytische Funktionen (1936)",

$$n(r, a) = n[r, 1/(f - a)]$$

is the number of  $a$ -points of  $f(z)$  which lie within and on the circumference of  $|z| = r$ , multiple  $a$ -points being counted with their order of multiplicity. Furthermore

$$N(r, a) = N\left(r, \frac{1}{f - a}\right) = \int_0^r \frac{n(t, a) - n(0, a)}{t} dt + n(0, a) \log r$$

$$N(r, \infty) = N(r, f).$$

Here we adopt the plane as opposed to the spherical definition of  $m(r, a)$ , *viz.*,

$$m(r, a) = m\left(r, \frac{1}{f - a}\right) = \frac{1}{2\pi} \int_0^{2\pi} \log^+ \left| \frac{1}{f(re^{i\phi}) - a} \right| d\phi$$

and

$$m(r, \infty) = m(r, f) = \frac{1}{2\pi} \int_0^{2\pi} \log^+ |f(re^{i\phi})| d\phi.$$

Then

$$T(r) = T(r, f) = m(r, f) + N(r, f)$$

is Nevanlinna's characteristic for the function  $f(z)$  and, for any complex  $a$ ,

$$T(r) = m(r, a) + N(r, a) + O(1).$$

The deficiency  $\delta(a)$  of the value  $a$  is defined by the equation

$$\delta(a) = \liminf_{r \rightarrow R} \frac{m(r, a)}{T(r)} = 1 - \limsup_{r \rightarrow R} \frac{N(r, a)}{T(r)}.$$

Plainly  $0 \leq \delta(a) \leq 1$ . A value  $a$  is said to be deficient if  $\delta(a) > 0$ .

The upper (or Valiron) deficiency of the value  $a$  is defined by

$$\Delta(a) = \limsup_{r \rightarrow R} \frac{m(r, a)}{T(r)} = 1 - \liminf_{r \rightarrow R} \frac{N(r, a)}{T(r)}$$

from which it follows that

$$0 \leq \delta(a) \leq \Delta(a) \leq 1.$$

For any function  $f(z)$  having  $T(r)$  equal to  $T(r, f)$  unbounded, deficiency of either type is an exceptional property. For such a function, and we shall confine ourselves exclusively to such functions, the distribution of  $a$ -points is anomalous if  $\Delta(a) > 0$ ; and *a fortiori* if  $\delta(a)$  is greater than 0. A value  $a$  for which  $\Delta(a) > 0$ , we call an exceptional value, and a value for which  $\Delta(a) = 0$ , a normal value of  $f(z)$ .

Defining by  $S$  the Riemann surface on which the function  $w = f(z)$  maps its domain of existence  $|z| < R \leq \infty$  and  $\sigma$  to be a positive number Collingwood mentions the result due to Teichmüller:

If over the domain  $|w - a| < \sigma$  (or  $1/|w| < \sigma$  if  $a = \infty$ ) the surface  $S$  has only schlicht sheets all of whose boundary points are internal points of  $S$ , then

$$m(r, a) = O(1)$$

and hence, if  $T(r)$  is unbounded,  $\Delta(a) = 0$ .

Proceeding further Collingwood puts the schlicht-condition theorem in the form which is more direct:

If, for a given complex  $a$  and  $\sigma > 0$ ,  $f(z)$  is schlicht in every domain  $G(a, \sigma)$  and if none of these domains is unbounded, then

$$m(r, a) = O(1)$$

is satisfied.

4. Recently Selberg has given a generalization of this theorem in the following form:

If over the domain  $|w - a| < \sigma$  (or  $|1/w| < \sigma$  if  $a = \infty$ ) the surface  $S$  consists of portions of not more than  $p$  sheets all of whose frontier points are internal points of  $S$ , then

$$m(r, a) < p \log r + \log^+ \frac{1}{\sigma} + O(1).$$

Collingwood has given a generalization of the theorems of Selberg and Teichmüller in the following theorem:

(i) Suppose that  $f(z)$  is meromorphic in  $|z| < R \leq \infty$  and that for a given  $a$  there is a positive  $\sigma(r)$  which is either constant or tends monotonically to zero as  $r$  tends to  $R$  and  $ap(r)$  satisfying  $0 \leq p(r) < \infty$  for all  $r < R$  such that  $R$  is a limit point of the set  $E = E[a, \sigma(r), p(r)]$ . Under these conditions we have, for all  $r \in E$ ,

$$(4.1) \quad m(r, a) < (\pi + \log r) p(r) + \log^+ \frac{1}{\sigma(r)} + O(1)$$

in the parabolic case  $R = \infty$ ; and

$$(4.2) \quad m(r, a) < [\pi + o(1)] p(r) + \log^+ \frac{1}{\sigma(r)} + O(1)$$

in the hyperbolic case  $R < \infty$ .

(ii) Suppose that in addition to the conditions specified in (i) the following condition is also satisfied, viz., (\*) there are non-negative numbers  $A < R$  and  $B < R$  such that for any  $r$  in  $A < r < R$  none of the domains  $G_\nu[r, a, \sigma(r)]$ , where  $\nu \leq \lambda(r)$ , whether bounded or not contains a closed curve which encloses the circumference  $|z| = B$ . Then for  $R$  and all  $r \in E$ ,

$$(4.3) \quad m(r, a) < \frac{\pi}{2} p(r) + \log^+ \frac{1}{\sigma(r)} + O(1).$$



The condition (\*) implies the weaker condition: (\*\*) there are non-negative numbers  $A < R$  and  $B < R$  such that if  $A < r \in E$  none of the domains  $G_\nu$ ,  $[r, a, \sigma(r)]$ , where  $\nu \leq \lambda(r)$ , contains a closed curve which encloses the circumference  $|z| = B$ .

5. We have attempted to obtain the generalizations of the formula which has been worked upon by Collingwood and others. Parreau has indicated one of the possible generalizations in a note in the *Comptes Rendus*. Milloux's work on the generalization also in the *Comptes Rendus* is noteworthy. We have investigated the generalization of the theorem but there may be certain specific conditions that would have to be imposed.

#### ACKNOWLEDGMENT

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# ON EXCEPTIONAL VALUES OF MEROMORPHIC FUNCTIONS—II

(A NOTE)

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(Communicated by Dr. P. L. Srivastava)

1. In a recent paper while studying the exceptional values of meromorphic functions we discussed the generalization of the following theorem due to E. F. Collingwood. We shall in the present paper investigate the proof of an inequality involved in the above.

2. Collingwood gave the theorem:

(i) Suppose that  $f(z)$  is meromorphic in  $|z| < R$  and that for a given  $a$  there is a positive  $\sigma(r)$  which is either constant or tends monotonically to zero as  $r$  tends to  $R$  and a  $p(r)$  satisfying  $0 \leq p(r) < \infty$  for all  $r < R$  such that  $R$  is the limit point of the set  $E = E[a, \sigma(r), p(r)]$ .

Under these conditions we have, for all  $r \in E$ ,

$$(2.1) \quad m(r, a) < (\pi + \log r) p(r) + \log^+ \frac{1}{\sigma(r)} + O(1)$$

in the parabolic case  $R = \infty$ , and

$$(2.2) \quad m(r, a) < [\pi + o(1)] p(r) + \log^+ \frac{1}{\sigma(r)} + O(1)$$

in the hyperbolic case  $R < \infty$ .

(ii) Suppose that in addition to the conditions specified in (i) the following condition is also satisfied, viz., (\*) there are non-negative numbers  $A < R$  and<sup>1</sup>  $B < R$  such that for any  $r$  in  $A < r < R$  none of the domains  $G_\nu[r, a, \sigma(r)]$ , where  $\nu \leq \lambda(r)$ , whether bounded or not contains a closed curve which encloses the circumference  $|z| = B$ . Then, for  $R \leq \infty$  and all  $r \in E$ ,

$$(2.3) \quad m(r, a) < \frac{\pi}{2} p(r) + \log^+ \frac{1}{\sigma(r)} + O(1).$$

The condition (\*) implies the weaker condition: (\*\*) there are non-negative numbers  $A < R$  and  $B < R$  such that if  $A < r \in r$  none of the domains  $G_\nu[r, a, \sigma(r)]$ , where  $\nu \leq \lambda(r)$ , contains a closed curve which encloses the circumference  $|z| = B$ .

3. The proof of the above theorem rests on the inequality (2.3) which depends in turn on the two conditions imposed, viz., (\*) and (\*\*). In order to prove (2.3), the other author has supposed that the condition (\*\*) is satisfied for  $a = \infty$ . Then given  $r_1 < R$ , there exists  $r_2$ , where  $r_1 < r_2 < R$ , such that for  $r_2 < r \in E$  the domains  $G_\nu(r) = G_\nu[r, \infty, \sigma(r)]$  all lie outside  $|z| = r_1$ . We may choose  $r_1 > B$  and  $r_2 > A$ . Then all the  $G_\nu(r)$ , if any exist for this value of  $r$ , lie outside  $|z| = B$  and none of them contains a closed curve enclosing the origin  $z = 0$ , which therefore lies in an unbounded domain  $D_r$  excluded from all the  $G_\nu(r)$ .

The author proceeding further uses the transformation

$$\zeta = \log z = \log r + i\phi$$

which maps the annulus  $r_1 < |z| < r'$ , cut along  $\gamma(r_1, r')$  upon a strip-like domain  $\mathcal{E}(r_1, r')$  bounded by two transforms of  $\gamma(r_1, r')$ , corresponding points of which are separated by a distance  $2\pi$ . Every  $G_\nu(r)$  is transformed into a finite closed domain  $F_\nu(\log r)$  contained in  $\mathcal{E}(r_1, r')$ , and the circumference  $|z| = r$  which intercepts all the  $G_\nu(r)$  is transformed into a cross-cut of  $\mathcal{E}(r_1, r')$  parallel to the  $\phi$ -axis and of length  $2\pi$ .

4. As the proof of the main theorem rests on the inequality (2.3), we have investigated if the proof of this can be obtained without imposing the conditions (\*) and (\*\*). We have also applied a few weaker conditions. It seems solvable that the inequality (2.3) can be proved by neglecting altogether the conditions (\*) and (\*\*), or else by subjecting to some weaker condition. At present we are investigating the proof of (2.3) by passing the Teichmüller-Selberg inequality.

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The author expresses his gratitude to his teacher, Dr. P. L. Srivastava, D.Phil. (Oxon.), Professor of Mathematics, University of Allahabad, for the guidance he has given him in this work.

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# ON EXCEPTIONAL VALUES OF MEROMORPHIC FUNCTIONS—III

(A NOTE)

BY YOGENDRA BEHARI LAL MATHUR

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(Communicated by Dr. P. L. Srivastava)

1. In the present note we propose to investigate an analogue of Inversen's Lemma for functions in the unit circle. This Lemma has been stated by E. F. Collingwood in the following form :

*Inversen's Lemma.*—If  $f(z)$  is meromorphic in  $|z| < \infty$  and of finite valency in an unbounded domain  $G(a, \sigma)$ , then, for any  $\sigma_1 < \sigma$ , the domains  $G(a, \sigma_1)$  contained in  $G(a, \sigma)$  are finite in number and all are bounded.

2. It is now necessary to introduce the notion of valency and of a level. For a given value of  $r$  the parts of the frontiers of the domains  $G(r, a, \sigma)$ , if any such domains exist, within the domain  $|z| < R \leq \infty$  consist of level curves on which  $|f(z) - a| = \sigma$ . We then say that  $\sigma$  is a level of positive valency relative to  $f(z)$  and  $a$  for this value of  $r$ . If no domain  $G(r, a, \sigma)$  exists, that is if  $|f(re^{i\phi} - a| \geq \sigma$  for all  $0 \leq \phi < 2\pi$  we say that  $\sigma$  is a null level relative to  $f|z$  and  $a$  for this value of  $r$ .

3. With the concept of level is associated a valency. For a given value of  $r$  the valency  $P(r, a, \sigma) = P[r, 1/(f - a), \sigma]$  of a level relative to  $f(z)$  and  $a$  is by definition, the maximum value of the valency of  $f(z)$  in any one of the domains  $G(r, a, \sigma)$ . Thus, denoting by  $p_\nu(r, a, \sigma)$  the valency of  $f(z)$  in a domain  $G_\nu(r, a, \sigma)$ ,

$$P(r, a, \sigma) = \max_{\nu \leq \lambda(r)} p_\nu(r, a, \sigma).$$

4. In the paper referred to above, Collingwood has defined certain sets determined by properties of a level relative to  $f(z)$  and  $a$ .  $V(a, \sigma, 0) = V[1/(f - a), \sigma, 0]$  is the set of values of  $r$  in  $0 \leq r \leq R \leq \infty$  for which  $\sigma$  is a null level relative to  $f(z)$  and  $a$ .  $V(a, \sigma, p) = V[1/(f - a), \sigma, p]$ ,  $0 \leq p < \infty$ , is the set for which  $\sigma$  is either a closed or open level relative to  $f(z)$  and  $a$  of valency  $P(r, a, \sigma) \leq p$ . It follows from this that

$$V(a, \sigma, p) = \sum_{q=0}^p V(a, \sigma, q).$$

The set for which  $\sigma$  is either a closed or open level relative to  $f(z)$  and  $a$  of finite, but not necessarily bounded, valency is defined by

$$\mathcal{B}(a, \sigma) = \mathcal{B}\left(\frac{1}{f-a}, \sigma\right) = \sum_{q=0}^{\infty} V(a, \sigma, q).$$

The complements of these sets with respect to the interval  $0 \leq r < R$  are denoted by  $CV(a, \sigma, 0)$ ,  $CV(a, \sigma, p)$  and  $C\mathcal{B}(a, \sigma)$  respectively. Then

$$CV(a, \sigma, p) = \prod_{q=0}^p CV(a, \sigma, q),$$

and

$$C\mathcal{B}(a, \sigma) = \prod_{p=0}^{\infty} CV(a, \sigma, p).$$

Again  $E(a, \sigma, p) = E[1/(f-a), \sigma, p]$ ,  $0 \leq p < \infty$

is the set in which  $\sigma$  is a closed level relative to  $f(z)$  and  $a$  of valency  $P(r, a, \sigma) \leq p$ , subject to the convention

$$E(a, \sigma, 0) = V(a, \sigma, 0),$$

whence it follows that

$$E(a, \sigma, p) = \sum_{q=0}^p E(a, \sigma, q).$$

The set for which  $\sigma$  is a closed level relative to  $f(z)$  and  $a$ , necessarily of finite valency, is defined by

$$\mathcal{F}(a, \sigma) = \mathcal{F}\left(\frac{1}{f-a}, \sigma\right) = \sum_{q=0}^{\infty} E(a, \sigma, q).$$

The complements of these sets are denoted when considered with respect to  $0 \leq r < R$ , by  $CE(a, \sigma, p)$  and  $C\mathcal{F}(a, \sigma)$ , where

$$CE(a, \sigma, p) = \prod_{q=0}^p CE(a, \sigma, q),$$

$$C\mathcal{F}(a, \sigma) = \prod_{q=0}^{\infty} CE(a, \sigma, q).$$

5. By definitions, the above author obtains the results

$$(5.1) \quad E(a, \sigma, p) \subseteq V(a, \sigma, p)$$

whence

$$(5.2) \quad \mathcal{F}(a, \sigma) \subseteq \mathcal{B}(a, \sigma)$$

and finally, when  $\sigma$  and  $p$  are replaced by  $\sigma(r)$  and  $p(r)$ , where  $0 < \sigma(r) < \infty$  and  $0 \leq p(r) < \infty$ , the following relations are established

$$(5.3) \quad E[a, \sigma(r), p(r)] \subseteq V[a, \sigma(r), p(r)],$$

$$(5.4) \quad \mathcal{F}[a, \sigma(r)] \subseteq \mathcal{B}[a, \sigma(r)].$$

6. We use Inversen's Lemma defined in §1 to obtain the relations complementary to (6.1) and (6.3) for the parabolic case when  $R = \infty$ . In the parabolic case it follows, if  $\sigma_1 < \sigma$  and  $0 < p < \infty$ , that

$$r \in V(a, \sigma, p) \text{ implies } r \in E(a, \sigma_1, p).$$

For every  $G(r, a, \sigma)$ , whether bounded or unbounded, contains only bounded domains  $G(a, \sigma_1)$  and these include all the  $G(r, a, \sigma_1)$ . Thus

$$V(a, \sigma, p) \subseteq E(a, \sigma_1, p)$$

Similarly if  $\sigma_1(r) < \sigma(r)$  and  $0 \leq p(r) < \infty$ ,

$$V[a, \sigma(r), p(r)] \subseteq E[a, \sigma_1(r), p(r)].$$

7. The proof of Inversen's Lemma depends upon the problem for parabolic surfaces due to Gross. We have tried to study an analogue of this lemma due to Inversen when the functions are situated in a particular region, the unit circle. The result of these investigations which will shortly be obtained in the final form will prove useful in study of the various particular cases of the function discussed above.

#### ACKNOWLEDGMENT

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# ON EXCEPTIONAL VALUES OF MEROMORPHIC FUNCTIONS—IV

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(Communicated by Dr. P. L. Srivastava)

## SUMMARY

1. In the present note it has been tried to determine the character of  $a$ , if  $f(z)$  is an integral function and  $\delta(a) > 0$ . It is considered that  $a$  ought to be an asymptotic value, and that the problem should be solvable.
2. The general reference is to E. F. Collingwood's paper and to the author's three previous papers.

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# ON A THEOREM OF PHRAGMEN LINDELÖF

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Phragmen and Lindelöf, D.<sup>1</sup> have proved the following theorem:—

THEOREM A.—If  $\phi(s)$  is regular and  $O(e^{\epsilon |t|})$ ,  $\epsilon$  being positive and arbitrarily small, in the strip  $\sigma_1 \leq \sigma \leq \sigma_2$ ,

and

$$\phi(\sigma_1 + it) = O(|t|^{k_1})$$

$$\phi(\sigma_2 + it) = O(|t|^{k_2})$$

then

$$\phi(\sigma + it) = O(|t|^{k(\sigma)}) \text{ uniformly for } \sigma_1 \leq \sigma \leq \sigma_2.$$

$k(\sigma)$  being any linear function of  $\sigma$  which takes the values  $k_1$  and  $k_2$  for  $\sigma = \sigma_1$  and  $\sigma = \sigma_2$ .

I have proved the following theorem:—

2. THEOREM 1.—If  $\phi(s)$  is regular and  $O(e^{k|t|})$ ,  $k$  being positive and finite, in the strip  $\sigma_1 \leq \sigma \leq \sigma_2$ , and

$$(2.1) \quad \phi(\sigma_1 + it) = O(e^{k_1 |t|})$$

$$(2.2) \quad \phi(\sigma_2 + it) = O(e^{k_2 |t|})$$

Then

$\phi(\sigma + it) = O(e^{k(\sigma)|t|})$  uniformly for  $\sigma_1 \leq \sigma \leq \sigma_2$ ,  $k(\sigma)$  being such a linear function of  $\sigma$  which takes the values  $k_1$  and  $k_2$  for  $\sigma = \sigma_1$  and  $\sigma = \sigma_2$ .

Suppose first that  $k_1 = 0$ ,  $k_2 = 0$ , so that  $\phi(s)$  is bounded for  $\sigma = \sigma_1$  and  $\sigma = \sigma_2$ . Let  $M$  be the upper bound of  $\phi(s)$  on these two lines and on the segment of the real axis between  $\sigma_1$  and  $\sigma_2$ . Let

$$(2.3) \quad g(s) = \phi(s) e^{\epsilon s^2} \quad \epsilon > 0$$

then

$$|g(s)| = (e^{\epsilon(\sigma^2 - t^2)} |\phi(s)|) = O(e^{-\epsilon t^2}) = O(1).$$

for  $\sigma = \sigma_1$  and  $\sigma = \sigma_2$ .

<sup>1</sup> Titchmarsh, E. C., *Theory of Functions*, Second Edition (1939), pp. 180-81.

Also  $|g(s)| \rightarrow 0$  as  $t \rightarrow \infty$ , since on  $t = T$ ,  $\sigma_1 \leq \sigma \leq \sigma_2$ , we have

$$g(s) = 0 (e^{-\epsilon T^2 + kT})$$

which  $\rightarrow 0$  as  $T \rightarrow \infty$  ( $k$  being finite).

$\therefore |g(s)| \leq M$  at all points of the rectangle  $(\sigma_1, \sigma_2), (0, T)$ .

Hence  $|g(S)| \leq M$  at all points of the half strip, i.e.,

$$|\phi(S)| \leq e^{\epsilon(t^2 - \sigma^2)} M$$

making  $\epsilon \rightarrow 0$ , it follows that  $|\phi(s)| \leq M$  for  $t > 0$ , and similarly for  $t < 0$ . This proves the theorem in a particular manner considered.

In the general case, let

$$(2.4) \quad F(S) = e^{\psi(s)(-is)}$$

where  $\psi(s)$  is any linear function of  $s$  say  $\psi(S) = as + b$ . This function is regular for  $\sigma_1 \leq \sigma \leq \sigma_2$ ,

$$\therefore |F(s)| = e^{R[\psi(s)(-is)]}$$

$$\text{and} \quad R[\psi(s)(-is)] = R[\{\psi(\sigma) + ait\}(t - i\sigma)]$$

$$= t\psi(\sigma) + a\sigma t$$

$$= [\psi(\sigma) + a\sigma]t = k(\sigma)t$$

where  $k(\sigma)$  is also a linear function of  $\sigma$ .

$$\therefore |F(S)| = e^{k(\sigma)|t|}.$$

Now suppose  $k(\sigma_1) = k_1$  and  $k(\sigma_2) = k_2$  and consider the function

$$(2.5) \quad G(s) = \frac{\phi(s)}{F(s)}.$$

This function satisfies the same conditions as  $\phi(s)$  did in the first part.

Hence  $G(s)$  is bounded in the strip and

$$\phi(s) = 0 (F(s)) = 0 (e^{k(\sigma)|t|}),$$

where  $k(\sigma)$  is such a linear function of  $\sigma$  which takes the values  $k_1$  and  $k_2$  for  $\sigma = \sigma_1$  and  $\sigma = \sigma_2$ .

3. The following Theorem is also true:—

THEOREM 2.—If  $\phi(S)$  is regular and  $O(e^{k_1 t_1 \beta^3})$  for  $k > 0$  and  $3 > \beta \geq 0$ , in the strip  $\sigma_1 \leq \sigma \leq \sigma_2$  and

$$(3.1) \quad \phi(\sigma_1 + it) = O(e^{k_1 t_1})$$

$$(3.2) \quad \phi(\sigma_2 + it) = O(e^{k_2 t_1})$$

Then

$$\phi(\sigma + it) = O(e^{k(\sigma) t_1})$$

uniformly for  $\sigma_1 \leq \sigma \leq \sigma_2$ ,  $k(\sigma)$  being such a linear function of  $\sigma$  which takes its values  $k_1$  and  $k_2$  for  $\sigma = \sigma_1$  and  $\sigma = \sigma_2$ .

*Proof.*—Suppose first that  $k_1 = 0$ ,  $k_2 = 0$ , so that  $\phi(s)$  is bounded for  $\sigma = \sigma_1$  and  $\sigma = \sigma_2$ . Let  $M$  be the upper bound of  $\phi(s)$  on these two lines and on the segment of the real axis between  $\sigma_1$  and  $\sigma_2$ . Let

$$(3.3) \quad g(S) = \phi(S) e^{\epsilon^S \alpha} \quad (\alpha > \beta, 3 > \alpha > 1)$$

$$\text{also } |e^{\epsilon^S \alpha}| = e^{\epsilon(\sigma^2 + t^2)\alpha/2} \cos\left(\alpha \tan^{-1} \frac{t}{\sigma}\right).$$

$$\therefore |g(s)| < |\phi(s)| e^{\epsilon t \alpha} \cos\left(\alpha \tan^{-1} \frac{t}{\sigma}\right)$$

$$\leq M e^{-\epsilon t \alpha} = O(1).$$

On the lines  $\sigma = \sigma_1$  and  $\sigma = \sigma_2$ . For when  $t \rightarrow \infty$  and  $\sigma = \sigma_1$ ,  $\cos\left(\alpha \tan^{-1} \frac{t}{\sigma}\right) < 0$

if  $3 > \alpha > 1$ , which is true.

Also  $|g(s)| \leq e^{-\epsilon t \alpha + k t \beta} \rightarrow 0$  as  $t \rightarrow \infty$  if  $\alpha > \beta$  ( $k$  being finite).

$\therefore |g(s)| \leq M$  at all points of the half strip, i.e.,

$|\phi(s)| \leq e^{\epsilon t \alpha} M$  in the upper half strip. Similarly, in the

lower half strip. Now making  $\epsilon \rightarrow 0$ , we get

$$|\phi(s)| \leq M \text{ in the whole strip } \sigma_1 \leq \sigma \leq \sigma_2.$$

The second part of the proof is the same as in Theorem 1.

Hence the Theorem is proved.

# TWO THEOREMS CONCERNING ANALYTIC FUNCTION OF AN ANALYTIC FUNCTION

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1. Carlson<sup>1</sup> has proved the following theorem:—

If  $f(z)$  is regular and of the form  $O(e^{k|z|})$ , where  $k < \pi$  for  $R(z) \geq 0$  and  $f(z) = 0$  for  $z = 0, 1, 2, \dots$

then  $f(z) \equiv 0$ .

I have proved the following theorem:—

2. THEOREM I.—If  $f(z)$  is regular and of the form  $O(|z|)$  for  $R(z) \leq 0'$  such that  $\phi[f(z)]$  is also regular in the half plane  $R(z) \geq 0'$  and

$$(2.1) \quad \phi[f(z)] = O(e^{k|f(z)|}), \quad k \text{ being finite.}$$

$$(2.2) \quad \phi[f(z)] = 0, \text{ for } z = 0, 1, 2, \dots$$

then  $\phi[f(z)] \equiv 0$ .

*Proof.*—Consider the function

$$(2.3) \quad F(z) = \phi[f(z)] \operatorname{cosec} \pi z.$$

On the circles  $|z| = n + \frac{1}{2}$ ,  $\operatorname{cosec} \pi z$  is bounded.

$$\text{Hence } |F(z)| \leq M(e^{k|f(z)|}) \leq Me^{k\epsilon|z|} = O(e^{\epsilon'|z|})$$

$\epsilon$  and  $\epsilon'$  are small and  $M$  any finite constant. Hence  $F(z) = O(e^{\epsilon'|z|})$  on these circles, and on the imaginary axis.

Since  $F(z)$  is regular, it follows that if  $n - \frac{1}{2} < |z| < n + \frac{1}{2}$ .

$$F(z) = O(e^{k\epsilon(n+\frac{1}{2})}) = O(e^{k\epsilon|z|}) = O(e^{\epsilon'|z|})$$

and so  $f(z)$  is of this form throughout  $R(z) \geq 0$ .

Also  $F(z) = O(e^{(\epsilon' - \pi)|z|}) = O(e^{-k'|z|})$ , where  $k' > 0$ , on  $R(z) = 0$ .

$\therefore$  By Riesz's Theorem

$$F(z) \equiv 0, \text{ i.e., } \phi[f(z)] \equiv 0.$$

## 2. THEOREM II. If

(2.1)  $\phi(z)$  and  $f(z)$  are analytic functions of  $z (= x + iy)$  in the strip  $|y| \leq k + \delta$ ,  $x \geq -\delta$ , where  $k$  and  $\delta$  are some positive numbers.

(2.2)  $\phi[f(z)]$  is also regular in the abovementioned strip and satisfies the inequality.

(2.2')  $\phi[f(z)] = O(e^{M|f(z)|})$ ,  $M > 0$  and finite, where  $f(z) = o(|z|)$  or  $|f(z)| < \epsilon|z|$ , ( $\epsilon$  being arbitrarily small), uniformly throughout this strip as  $|z| \rightarrow \infty$ .

(2.3) All the derivatives of  $f(x)$  are bounded and not equal to zero at origin.

(2.4)  $F(S) = \int_0^\infty \phi[f(z)] e^{-sz} dz$  which is certainly an analytic function of  $S$  in the half-plane  $\sigma \geq \delta$ ,  $\delta > 0$ , possesses an infinity of zeros

in this half-plane; Then  $F(S) \equiv 0$ .

*Proof.*—Suppose  $s_1, s_2, \dots, s_n$  are the zeros of  $F(S)$ . Then since the zeros of analytic function are isolated,  $s_n \rightarrow \infty$  as  $n \rightarrow \infty$ , in the half-plane  $\sigma \geq \delta_1 > 0$ .

Take a point  $P(x)$  on the real axis in the  $z$ -plane. If  $x$  be sufficiently large, then we can describe a circle  $C$  of radius  $e^{-\epsilon x}$  round  $P$  such that  $C$  lies entirely within the strip defined in (2.1),  $\epsilon$  being an arbitrarily small positive number. By Cauchy's Theorem we shall have taken the  $\mu$ th derivative

$$\phi^\mu[f(x)] = \frac{\mu!}{2\pi i} \int_C \frac{\phi[f(z)]}{(z-x)^{\mu+1}} dz.$$

so that

$$(2.5) \quad \phi^\mu[f(x)] \leq K\mu! e^{\mu\epsilon x + \epsilon'x} = O\{e^{(\epsilon' + \mu\epsilon)x}\}$$

for  $\mu = 0, 1, 2, \dots$

Now consider

$$sF(s) = s \int_0^\infty \phi[f(x)] e^{-sx} dx,$$

the integral being absolutely and uniformly convergent throughout the half-plane  $\sigma \geq \epsilon + \delta_1 > 0$ .

Integrating by parts, we have if  $\sigma \geq \delta_1 > 0$

$$\begin{aligned}
 sF(S) &= \left\{ -\phi[f(x)] e^{-sx} \right\}_0^\infty + \int_0^\infty \phi'[f(x)] f'(x) e^{-sx} dx. \\
 s \cdot F(S) &= \phi[f(0)] + \int_0^\infty \phi'[f(x)] f'(x) e^{-sx} dx \\
 &= \phi[f(0)] + \left\{ \frac{-\phi'[f(x)] f'(x) e^{-sx}}{s} \right\}_0^\infty + \\
 &\quad + \frac{1}{s} \int_0^\infty \left\{ \phi''[f(x)] [f'(x)]^2 + \phi'[f(x)] [f''(x)] \right\} e^{-sx} dx. \\
 (2.6) \quad &= \phi[f(0)] + \frac{\phi'[f(0)] f'(0)}{s} + \frac{1}{s} \int_0^\infty \left\{ \phi''[f(x)] [f'(x)]^2 \right. \\
 &\quad \left. + \phi'[f(x)] [f''(x)] \right\} e^{-sx} dx.
 \end{aligned}$$

Now the integral

$$\int_0^\infty e^{-sx} \left[ \left\{ \phi''[f(x)] [f'(x)]^2 \right\} + \left\{ \phi'[f(x)] \right\} \left\{ f''(x) \right\} \right] dx$$

being absolutely and uniformly convergent throughout the half-plane  $\sigma \geq \delta_1 > 0$ , is bounded throughout this half-plane. So that the right side of (2.6) tends to  $\phi[f(0)]$  as  $s \rightarrow \infty$ , in the half-plane. But by hypothesis  $sF(s)$  also vanishes for a sequence of values of  $s$  in the same half-plane whose limit is infinity.

Hence  $\phi[f(0)] = 0$ . That is,

$$(2.7) \quad sF(s) = \int_0^\infty \phi'[f(x)] f'(x) e^{-sx} dx = F_1(s) \text{ (say).}$$

Now applying the same argument to  $F_1(s)$  as we did to  $F(s)$  above, we can prove that  $\phi'[f(0)] = 0$ . Similarly, we can prove that  $\phi''[f(0)] = \phi'''[f(0)] = \dots = 0$ . It follows, therefore, that the function  $\phi[f(x)]$  is analytic in the neighbourhood of the origin, and so  $\phi[f(z)]$  is identically zero. Consequently  $F(s)$  vanishes identically. This proves the theorem.

I am indebted to Dr. P. L. Srivastava, under whose guidance, these results were obtained.

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# A STUDY OF A GENERALISATION OF THE LAPLACE'S INTEGRAL

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(Communicated by Dr. R. S. Varma)

## 1. Generalisations of the Laplace's Integral

$$f(p) = p \int_0^{\infty} e^{-px} h(x) dx \quad (1)$$

have been given by Meijer,<sup>1</sup> Boas,<sup>2</sup> Varma<sup>3</sup> and other writers. The Laplace-Stieltjes Integral

$$f(p) = p \int_0^{\infty} e^{-px} d\alpha(x) \quad (2)$$

which reduces to (1) when  $\alpha(x)$  is absolutely continuous is of comparatively recent origin and is at present engaging the attention of several workers. Dr. R. S. Varma<sup>4</sup> has given a generalisation of (2) in the form

$$f(p) = p \int_0^{\infty} (px)^{m-\frac{1}{2}} e^{-\frac{1}{2}px} W_{k,m}(px) d\alpha(x), \quad (3)$$

where  $\alpha(x)$  denotes a function of bounded variation in  $0 \leq x \leq R$  for every  $R$ .

When  $\alpha(x)$  is absolutely continuous, (3) yields

$$f(p) = p \int_0^{\infty} (px)^{m-\frac{1}{2}} e^{-\frac{1}{2}px} W_{k,m}(px) h(x) dx, \quad (4)$$

where  $d\alpha(x) = h(x) dx$ .

The integral (1) has been the subject of intensive study for the last fifty years or more under the name of Operational Calculus and is symbolically written as  $f(p) \doteq h(x)$ .

<sup>1</sup> Meijer, (9).

<sup>2</sup> Boas, (1).

<sup>3</sup> Varma, (13).

<sup>4</sup> Varma, (14).



The object of this paper is to develop the transform based on the integral (4) which we represent symbolically as

$$f(p) \stackrel{v}{=} h(x).$$

$f(p)$  will be called the image of  $h(x)$  and  $h(x)$  the original of  $f(p)$ .

When  $k = -m + \frac{1}{2}$ , (4) reduces to (1) on account of the identity

$$W_{-m+\frac{1}{2}, m}(x) \equiv x^{-m+\frac{1}{2}} e^{-\frac{1}{2}x} \quad (5)$$

It is easily seen that a large number of the rules of ordinary Operational Calculus hold for this transform also.

2. We now find the images of a few functions which we shall require in our investigations later on.

(i) Taking in (4)

$$h(x) = e^{-ax} x^v$$

and using Goldstein's integral<sup>5</sup>

$$\begin{aligned} \int_0^\infty x^{l-1} e^{-(\frac{1}{2}+a^2)x} W_{k,m}(x) dx &= \frac{\Gamma(l+m+\frac{1}{2}) \Gamma(l-m+\frac{1}{2})}{\Gamma(l-k+1)} \\ &\times {}_2F_1\left(l+m+\frac{1}{2}, l-m+\frac{1}{2}; l-k+1; -a^2\right) \end{aligned} \quad (6)$$

we find

$$\begin{aligned} \text{(I.1)} \quad f(p) &= \frac{\Gamma(v+1) \Gamma(v+2m+1)}{\Gamma(v+m-k+3/2) p^v} \\ &\times {}_2F_1\left(v+1, v+2m+1; v+m-k+3/2; -\frac{a}{p}\right), \end{aligned}$$

$$R(v) > -1, R(v+2m) > -1.$$

(ii) If we take

$$h(x) = x^{c-2m-1} {}_3F_2\left(\frac{1}{2}-\lambda+\mu, \frac{1}{2}-\lambda-\mu, \frac{1}{2}+c-k-m; c, c-2m; -x\right),$$

then by virtue of the integral<sup>6</sup>

$$\begin{aligned} \int_0^\infty e^{-\frac{1}{2}t} t^{c-m-3/2} W_{k,m}^{(t)} {}_3F_2\left(\frac{1}{2}-\lambda+\mu, \frac{1}{2}-\lambda-\mu, \frac{1}{2}+c-k-m; c, c-2m; -\frac{t}{z}\right) dt \\ = \frac{\Gamma(c) \Gamma(c-2m)}{\Gamma(\frac{1}{2}+c-k-m)} e^{\frac{1}{2}z} z^{-\lambda} W_{\lambda,\mu}(z) \end{aligned} \quad (7)$$

<sup>5</sup> Goldstein, (5).

<sup>6</sup> Erdelyi, (3).

we get

$$(I.2) \quad f(p) = \frac{\Gamma(c) \Gamma(c-2m)}{\Gamma(\frac{1}{2} + c - k - m)} p^{2m-c-\lambda+1} e^{\frac{1}{2}p} W_{\lambda, \mu}(p),$$

$$R(c) > 0, R(c-2m) > 0, R(p) > 0.$$

In particular when  $c = \frac{1}{2} - \lambda - \mu$ , we have

$$(I.3) \quad x^{-\lambda-\mu-2m-\frac{1}{2}} {}_2F_1\left(\frac{1}{2}-\lambda+\mu, 1-\lambda-\mu-k-m; \frac{1}{2}-\lambda-\mu-2m; -x\right) \\ \frac{v}{v} \frac{\Gamma(\frac{1}{2}-\lambda-\mu) \Gamma(\frac{1}{2}-\lambda-\mu-2m)}{\Gamma(1-\lambda-\mu-k-m)} p^{2m+\mu+\frac{1}{2}} e^{\frac{1}{2}p} W_{\lambda, \mu}(p).$$

If in (I.3) we take  $\mu = -m$ , we get

$$(I.4) \quad x^{-\lambda-m-\frac{1}{2}} (1+x)^{\kappa+\lambda-1} \frac{v}{v} \frac{\Gamma(\frac{1}{2}-\lambda+m) \Gamma(\frac{1}{2}-\lambda-m)}{\Gamma(1-\lambda-k)} \\ \times p^{m+\frac{1}{2}} e^{\frac{1}{2}p} W_{\lambda, m}(p),$$

$$R(\frac{1}{2}-\lambda \pm m) > 0, R(p) > 0.$$

(iii) Next taking

$$h(x) = x^{v-1} {}_rF_s(a_1, \dots, a_r; \beta_1, \dots, \beta_s; \pm x)$$

and using the integral<sup>7</sup>

$$\int_0^\infty u^{l-1} e^{-\frac{1}{2}u} W_{k, m}(u) {}_rF_s(a_1, \dots, a_r; \beta_1, \dots, \beta_s; -cu) du \\ = \frac{\Gamma(l+m+\frac{1}{2}) \Gamma(l-m+\frac{1}{2})}{\Gamma(l-k+1)} {}_{r+2}F_{s+1}\left(\begin{matrix} a_1, \dots, a_r, l+m+\frac{1}{2}, l-m+\frac{1}{2} \\ \beta_1, \dots, \beta_s, l-k+1 \end{matrix}; -c\right) \quad (8)$$

we have

$$(I.5) \quad f(p) = \frac{\Gamma(v) \Gamma(v+2m)}{\Gamma(v+m-k+\frac{1}{2}) p^{v-1}} \\ \times {}_{r+2}F_{s+1}\left(\begin{matrix} a_1, \dots, a_r, v, v+2m \\ \beta_1, \dots, \beta_s, v+m-k+\frac{1}{2} \end{matrix}; \pm \frac{1}{p}\right)$$

$$R(v) > 0, R(v+2m) > 0, R(p) > 0 \text{ when } r < s; \text{ if } r = s, \text{ then}$$

$$R(p) > 1.$$

<sup>7</sup>Sinha, (12).

3. In this section we give a theorem on the transform based on the integral (4) and apply it to evaluate certain infinite integrals.

THEOREM I.—If

$$f(p) \frac{v}{p} h(x) \text{ and } p^{2-l} h(p) \doteq g(x),$$

then

$$f(p) = \frac{\Gamma(l) \Gamma(l+2m)}{p^{l-1} \Gamma(l+m-k+\frac{1}{2})} \int_0^\infty {}_2F_1 \left( l, l+2m; l+m-k+\frac{1}{2}; -\frac{t}{p} \right) \times g(t) dt,$$

provided that  $R(p) > 0$ ,  $R(l) > 0$ ,  $R(l+2m) > 0$ ,  $R(\mu+1) > 0$ ,  $R(v-l+1) < 0$ , and  $R(v-l-2m+1) < 0$  where  $g(t) = 0(t^\mu)$  for small  $t$  and  $g(t) = 0(t^\nu)$  for large  $t$ .

*Proof.*—By definition, we have

$$f(p) = p \int_0^\infty (px)^{m-\frac{1}{2}} e^{-\frac{1}{2}px} W_{k,m}(px) h(x) dx$$

and

$$x^{2-l} h(x) = x \int_0^\infty e^{-xt} g(t) dt.$$

Hence

$$\begin{aligned} f(p) &= p \int_0^\infty (px)^{m-\frac{1}{2}} e^{-\frac{1}{2}px} W_{k,m}(px) x^{l-1} dx \int_0^\infty e^{-xt} g(t) dt \\ &= \frac{1}{p^{l-1}} \int_0^\infty g(t) dt \int_0^\infty e^{-(\frac{1}{2}+\frac{t}{p})s} s^{l+m-3/2} W_{k,m}(s) ds, \end{aligned}$$

on changing the order of integration and affecting a slight change of variable. On evaluating the second integral with the help of (6) the theorem follows immediately.

In order to justify the change in the order of integration, suppose that

$$\theta(x) = x^{l+m-3/2} e^{-\frac{1}{2}px} W_{k,m}(px) \int_0^A e^{-xt} g(t) dt,$$

where  $A$  is small, and

$$\begin{aligned} \phi(t) &= g(t) \int_0^\infty s^{l+m-3/2} e^{-(\frac{1}{2}+\frac{t}{p})s} W_{k,m}(s) ds \\ &= \frac{\Gamma(l) \Gamma(l+2m)}{\Gamma(l+m-k+\frac{1}{2})} {}_2F_1 \left( l, l+2m; l+m-k+\frac{1}{2}; -\frac{t}{p} \right) g(t). \end{aligned}$$

Now

$$W_{k,m}(x) = 0 \quad (x^{\frac{1}{2} \pm m}) \text{ for small } x, \quad (9)$$

and

$$W_{k,m}(x) \sim x^k e^{-\frac{1}{2}x} \text{ for large } x. \quad (10)$$

Hence, if  $g(t) = 0(t^\mu)$  for small  $t$  where  $R(\mu) > -1$ ,  $\theta(x)$  is uniformly convergent for  $x \geq 0$  provided that  $R(l-1) > 0$ ,  $R(l+2m-1) > 0$ . Also  $\phi(t)$  is uniformly convergent for  $0 \leq t \leq p$  where  $R(p) > 0$  and  $R(\mu) > 0$ .

Next consider the integral

$$I = \int_T^\infty g(t) dt \int_{T'}^\infty e^{-(\frac{1}{2} + \frac{t}{p})s} s^{l+m-3/2} W_{k,m}(s) ds.$$

For large values of  $t$  and  $x$ ,  $I$  does not exceed a constant multiple of

$$\int_T^\infty |g(t)| dt \int_{T'}^\infty |e^{-(\frac{1}{2} + \frac{t}{p})s} s^{k+l+m-3/2}| ds$$

which tends to zero as  $T$  and  $T'$  independently tend to infinity provided that  $g(t)$  is of the order of  $t^\nu$  for large  $t$  and  $R(p) > 0$ . Thus the inversion of the order of integration is justified under the conditions  $R(\mu) > 0$ ,  $R(l-1) > 0$ ,  $R(l+2m-1) > 0$ ,  $R(p) > 0$ . Moreover the resulting integral is convergent at infinity when  $R(\nu-l+1) < 0$ ,  $R(\nu+2m-l+1) < 0$ .

By the principle of analytic continuation the conditions on  $l$ ,  $m$  and  $\mu$  may be relaxed to those stated along with the theorem.

*Corollary.*—When  $k = -m + \frac{1}{2}$ , the theorem reduces to one given by Shastri.<sup>8</sup>

4. We proceed to illustrate the theorem by a few examples.

*Example 1.*—Taking (I.1)

$$h(x) = e^{-ax} x^\nu$$

$$\begin{aligned} & \frac{\nu}{v} \frac{\Gamma(\nu+1) \Gamma(\nu+2m+1)}{\Gamma(\nu+m-k+3/2)} {}_2F_1\left(\nu+1, \nu+2m+1; \right. \\ & \qquad \qquad \qquad \left. \nu+m-k+3/2; -\frac{a}{p}\right) \\ & = f(p), \quad R(\nu) > -1, \quad R(\nu+2m) > -1, \end{aligned}$$

<sup>8</sup> Shastri, (11).

we have

$$p^{2-l} h(p) = p^{\nu-l+2} e^{-ap} \\ \doteq \frac{(x-a)^{\nu-2}}{\Gamma(l-\nu-1)}, \quad x > a, \quad R(l-\nu-1) > 0,$$

by virtue of a well-known operational relation.<sup>9</sup>

Hence the theorem gives

$$\frac{\Gamma(\nu+1) \Gamma(\nu+2m+1)}{\Gamma(\nu+m-k+\frac{3}{2})} {}_2F_1\left(\nu+1, \nu+2m+1; \right. \\ \left. \nu+m-k+\frac{3}{2}; -\frac{a}{p}\right) \\ = \frac{\Gamma(l) \Gamma(l+2m)}{\Gamma(l+m-k+\frac{1}{2}) p^{l-\nu-1}} \int_a^\infty {}_2F_1(l, l+2m; l+m-k+\frac{1}{2}; -t/p) \\ \times (t-a)^{l-\nu-2} dt.$$

On substituting  $t-a=ps$  and replacing  $l$  by  $a$ ,  $l+2m$  by  $b$ ,  $l+m-k+\frac{1}{2}$  by  $c$ ,  $l-\nu-1$  by  $r$  and  $-a/p$  by  $z$ , the result takes the form<sup>10</sup>

$$\frac{\Gamma(r) \Gamma(a-r) \Gamma(b-r)}{\Gamma(c-r)} {}_2F_1(a-r, b-r; c-r; z) \\ = \frac{\Gamma(a) \Gamma(b)}{\Gamma(c)} \int_0^\infty {}_2F_1(a, b; c; z-s) s^{r-1} ds,$$

$$R(a-r) > 0, \quad R(b-r) > 0, \quad R(r) > 0.$$

*Example 2.* Starting with (I.4)

$$h(x) = x^{-\lambda-m-\frac{1}{2}} (1+x)^{k+\lambda-1} \\ \doteq \frac{\nu}{v} \frac{\Gamma(\frac{1}{2}-\lambda+m) \Gamma(\frac{1}{2}-\lambda-m)}{\Gamma(1-k-\lambda)} p^{m+\frac{1}{2}} e^{\frac{1}{2}p} W_{\lambda, m}(p) \\ = f(p), \quad R(\frac{1}{2}-\lambda \pm m) > 0,$$

<sup>9</sup> McLachlan, (7), p. 18.

<sup>10</sup> Copson, (2), p. 268.

we have

$$\begin{aligned} p^{2-l} h(p) &= p^{3/2-l-\lambda-m} (1+p)^{k+\lambda-1} \\ &\doteq \frac{x^{l+m-k-\frac{1}{2}}}{\Gamma(l+m-k+\frac{1}{2})} {}_1F_1(1-k-\lambda; l+m-k+\frac{1}{2}; -x) \\ &= g(x), \quad R(l+m-k+\frac{1}{2}) > 0. \end{aligned}$$

Applying the theorem we get the following integral representation for Whittaker function.

$$\begin{aligned} W_{\lambda, m}(p) &= \frac{\Gamma(l) \Gamma(l+2m) \Gamma(1-k-\lambda) p^{\frac{1}{2}-m-l} e^{-\frac{1}{2}p}}{\Gamma(\frac{1}{2}-\lambda+m) \Gamma(\frac{1}{2}-\lambda-m) \Gamma^2(l+m-k+\frac{1}{2})} \\ &\times \int_0^\infty t^{l+m-k-\frac{1}{2}} {}_2F_1(l, l+2m; l+m-k+\frac{1}{2}; -t/p) \times \\ &\times {}_1F_1(1-k-\lambda; l+m-k+\frac{1}{2}; -t) dt, \end{aligned} \quad (11)$$

$$R(l) > 0, \quad R(l+2m) > 0, \quad R(\frac{1}{2}-\lambda \pm m) > 0, \quad R(l+m-k+\frac{1}{2}) > 0,$$

$$R(p) > 0.$$

The conditions  $R(l) > 0$  and  $R(l+2m) > 0$  may be waived by analytic continuation.

Taking  $\lambda = 0$  and using

$$W_{0, m}(x) = \sqrt{\frac{x}{\pi}} K_m(\frac{1}{2}x)$$

we get

$$\begin{aligned} K_m(\frac{1}{2}p) &= \frac{\Gamma(l) \Gamma(l+2m) \Gamma(1-k) \cos m\pi e^{-\frac{1}{2}p} p^{-l-m}}{\sqrt{\pi} \Gamma^2(l+m-k+\frac{1}{2})} \\ &\times \int_0^\infty t^{l+m-k-\frac{1}{2}} {}_2F_1(l, l+2m; l+m-k+\frac{1}{2}; -t/p) \times \\ &\times {}_1F_1(1-k; l+m-k+\frac{1}{2}; -t) dt, \end{aligned} \quad (12)$$

valid for  $|R(m)| < \frac{1}{2}$ ,  $R(l+m-k+\frac{1}{2}) > 0$ ,  $R(p) > 0$ .

Next putting  $\lambda = \frac{1}{2}\nu + \frac{1}{4}$ ,  $m = \frac{1}{4}$  and applying

$$W_{\frac{1}{2}\nu+\frac{1}{4}, \frac{1}{4}}(x) = 2^{-\frac{1}{2}\nu} x^{\frac{1}{2}} D_\nu(\sqrt{2}x)$$

we get

$$D_\nu(\sqrt{2p}) = \frac{\Gamma(l) \Gamma(l + \frac{1}{2}) \Gamma(\frac{3}{4} - \frac{1}{2}\nu - k) 2^{-\frac{1}{2}\nu-1} e^{-\frac{1}{2}p} p^{-l}}{\sqrt{\pi} \Gamma(-\nu) \Gamma^2(l - k + \frac{3}{4})} \\ \times \int_0^\infty {}_2F_1(l, l + \frac{1}{2}; l - k + \frac{3}{4}; -t/p) \\ \times {}_1F_1(\frac{3}{4} - k - \frac{1}{2}\nu; l - k + \frac{3}{4}; -t) t^{l-k-\frac{1}{4}} dt, \quad (13)$$

valid for  $R(l - k + \frac{3}{4}) > 0$ ,  $R(\nu) < 0$ ,  $R(p) > 0$ .

Since the Kummer's function  ${}_1F_1$  can be expressed in terms of Whittaker function  $M_{k,m}$ , Bessel function  $I_\nu$ , Laguerre, Sonine and Abel polynomials, incomplete Gamma function and various other functions, (11), (12) and (13) will give us by suitable choice of  $l$  and  $k$  integral representations involving these functions. These are, however, left for the reader.

The very special cases of (11) when (i)  $l = \frac{1}{2} - \lambda - m$  and (ii)  $k = -m + \frac{1}{2}$  have respectively been given by Meijer<sup>11</sup> and Hari Shanker.<sup>12</sup>

*Example 3.*—Taking<sup>13</sup>

$$g(x) = x^{-a-1} {}_1F_1(\beta; \gamma; -1/x) \\ = \frac{\Gamma(\gamma) \Gamma(\beta - a) \Gamma(a)}{\Gamma(\beta) \Gamma(\gamma - a)} p {}_1F_2(\beta - a; \gamma - a, 1 - a; p) \\ + p^{1+a} \Gamma(-a) {}_1F_2(\beta; \gamma, 1 + a; p) \\ = p^{2-l} h(p), \quad R(\beta - a) > 0, \quad a \text{ is not an integer or zero.}$$

we have

$$h(x) = \frac{\Gamma(\gamma) \Gamma(\beta - a) \Gamma(a)}{\Gamma(\beta) \Gamma(\gamma - a)} x^{l-1} {}_1F_2(\beta - a; \gamma - a, 1 - a; x) \\ + x^{l+a-1} \Gamma(-a) {}_1F_2(\beta; \gamma, 1 + a; x) \\ \frac{v}{v} \frac{\Gamma(\gamma) \Gamma(\beta - a) \Gamma(a) \Gamma(l) \Gamma(l + 2m) p^{l-l}}{\Gamma(\beta) \Gamma(\gamma - a) \Gamma(l + m - k + \frac{1}{2})}$$

<sup>11</sup> Meijer, (8)

<sup>12</sup> Harishanker, (6).

<sup>13</sup> Gupta, (4).

$$\times {}_3F_3(l, l+2m, \beta-a; l+m-k+\frac{1}{2}, \gamma-a, 1-a; 1/p)$$

$$+ \frac{\Gamma(-a)\Gamma(l+a)\Gamma(l+a+2m)}{\Gamma(l+a+m-k+\frac{1}{2})} p^{1-l-a}$$

$$\times {}_3F_3(l+a, l+a+2m, \beta; l+a+m-k+\frac{1}{2}, \gamma, 1+a; 1/p),$$

on term by term interpretation with the help of (I.5).

Hence by the theorem we get after replacing  $l$  by  $a$ ,  $l+2m$  by  $b$  and  $l+m-k+\frac{1}{2}$  by  $c$  and  $1/p$  by  $p$ ,

$$\begin{aligned} & \frac{\Gamma(a)\Gamma(b)}{\Gamma(c)} \int_0^\infty t^{-a-1} {}_2F_1(a, b; c; -tp) {}_1F_1(\beta; \gamma; -1/t) dt \\ &= \frac{\Gamma(a)\Gamma(b)\Gamma(a)\Gamma(\gamma)\Gamma(\beta-a)}{\Gamma(c)\Gamma(\beta)\Gamma(\gamma-a)} {}_3F_3(a, b, \beta-a; c, \gamma-a, 1-a; p) \\ &+ \frac{\Gamma(-a)\Gamma(a+a)\Gamma(b+a)}{\Gamma(c+a)} p^a \\ & {}_3F_3(a+a, b+a, \beta; \gamma, c+a, 1+a; p) \end{aligned} \quad (14)$$

valid for  $R(a) > 0$ ,  $R(b) > 0$ ,  $R(a+a) > 0$ ,  $R(b+a) > 0$ ,  $R(\beta-a) > 0$ ,  $R(p) > 0$ ,  $a$  is not an integer or zero.

The first two conditions may be waived by analytic continuation.

If  $p = 0$ , (14) is valid when  $R(a) > 0$ ,  $R(\beta-a) > 0$ .

In particular taking  $\beta = \gamma$  and substituting  $t = \frac{1}{px}$ , we get

$$\begin{aligned} & \frac{\Gamma(a)\Gamma(b)}{\Gamma(c)} \int_0^\infty e^{-px} x^{a-1} {}_2F_1(a, b; c; -1/x) dx \\ &= p^{-a} \frac{\Gamma(a)\Gamma(b)\Gamma(a)}{\Gamma(c)} {}_2F_2(a, b; c, 1-a; p) \\ &+ \frac{\Gamma(a+a)\Gamma(b+a)\Gamma(-a)}{\Gamma(c+a)} {}_2F_2(a+a, b+a; c+a, 1+a; p) \end{aligned}$$



from which it follows that

$$\begin{aligned} x^{a-1} {}_2F_1(a, b; c; -1/x) &\doteq \Gamma(a) p^{1-a} {}_2F_2(a, b; c, 1-a; p) \\ &+ \frac{\Gamma(a+a) \Gamma(b+a) \Gamma(c) \Gamma(-a)}{\Gamma(a) \Gamma(b) \Gamma(c+a)} \times \\ &\times p {}_2F_2(a+a, b+a; c+a, 1+a; p), \end{aligned} \quad (15)$$

$R(a+a) > 0$ ,  $R(b+a) > 0$ ,  $R(p) > 0$ ,  $a$  is not an integer or zero.

We now point out a limiting form of (14). Replace  $p$  by  $p/a$  and make  $a$  tend to infinity. Since

$$\lim_{a \rightarrow \infty} {}_2F_1(a, \beta; \gamma; -x/a) = {}_1F_1(\beta; \gamma; -x)$$

and

$$\lim_{a \rightarrow \infty} \frac{\Gamma(a+\lambda)}{\Gamma(a) a^\lambda} = 1$$

we get at once

$$\begin{aligned} &\int_0^\infty t^{a-1} {}_1F_1(b; c; -tp) {}_1F_1(\beta; \gamma; -1/t) dt \\ &= \frac{\Gamma(a) \Gamma(\gamma) \Gamma(\beta-a)}{\Gamma(\beta) \Gamma(\gamma-a)} {}_2F_3(b, \beta-a; c, \gamma-a, 1-a; p) \\ &+ \frac{\Gamma(b+a) \Gamma(c) \Gamma(-a)}{\Gamma(b) \Gamma(c+a)} p^a \\ &{}_2F_3(b+a, \beta; c+a, \gamma, 1+a; p), \end{aligned} \quad (16)$$

$R(\beta-a) > 0$ ,  $R(b+a) > 0$ ,  $R(p) > 0$ ,  $a$  is not an integer or zero. If  $p=0$ , then  $R(a) > 0$ ,  $R(\beta-a) > 0$ .

*Example 4.*—Taking<sup>14</sup>

$$\begin{aligned} g(x) &= x^{\frac{1}{2}\lambda-\mu-1} J_\lambda\left(\frac{2}{\sqrt{x}}\right) \\ &\doteq \frac{\Gamma(-\mu)}{\Gamma(1+\lambda)} p^{1+\mu} {}_0F_2(1+\mu, 1+\lambda; p) \\ &+ \frac{\Gamma(\mu)p}{\Gamma(\lambda-\mu+1)} {}_0F_2(1-\mu, 1-\mu+\lambda; p) = p^{2-l} h(p), \end{aligned}$$

<sup>14</sup> Gupta, (4).

we have

$$\begin{aligned}
 h(x) &= \frac{\Gamma(-\mu)}{\Gamma(1+\lambda)} x^{\lambda+\mu-1} {}_0F_2(1+\mu, 1+\lambda; x) \\
 &\quad + \frac{\Gamma(\mu)}{\Gamma(\lambda-\mu+1)} x^{\lambda-1} {}_0F_2(1-\mu, 1-\mu+\lambda; x) \\
 &\quad + \frac{v}{v} \frac{\Gamma(-\mu) \Gamma(l+\mu) \Gamma(l+2m+\mu)}{\Gamma(1+\lambda) \Gamma(l+\mu+m-k+\frac{1}{2})} p^{1-l-\mu} \\
 &\quad \times {}_2F_3(l+\mu, l+2m+\mu; 1+\mu, 1+\lambda, l+\mu+m-k+\frac{1}{2}; 1/p) \\
 &\quad + \frac{\Gamma(\mu) \Gamma(l) \Gamma(l+2m)}{\Gamma(\lambda-\mu+1) \Gamma(l+m-k+\frac{1}{2})} p^{1-l} \\
 &\quad \times {}_2F_3(l, l+2m; 1-\mu, 1-\mu+\lambda, l+m-k+\frac{1}{2}; 1/p) \\
 &= f(p).
 \end{aligned}$$

Hence by the theorem, after replacing  $l$  by  $\alpha$ ,  $l+2m$  by  $\beta$ ,  $l+m-k+\frac{1}{2}$  by  $\gamma$ , and  $p$  by  $1/p$ , we get

$$\begin{aligned}
 &\int_0^\infty t^{\lambda-\mu-1} {}_2F_1(\alpha, \beta; \gamma; -pt) J_\lambda\left(\frac{2}{\sqrt{t}}\right) dt \\
 &= \frac{\Gamma(-\mu) \Gamma(\alpha+\mu) \Gamma(\beta+\mu) \Gamma(\gamma)}{\Gamma(1+\lambda) \Gamma(\gamma+\mu) \Gamma(\alpha) \Gamma(\beta)} p^\mu \\
 &\quad \times {}_2F_3(\alpha+\mu, \beta+\mu; 1+\mu, 1+\lambda, \gamma+\mu; p) \\
 &\quad + \frac{\Gamma(\mu)}{\Gamma(\lambda-\mu+1)} {}_2F_3(\alpha, \beta; 1-\mu, 1-\mu+\lambda, \gamma; p). \quad (17)
 \end{aligned}$$

By the principle of analytic continuation, this is valid when

$$R(\alpha+\mu) > 0, R(\beta+\mu) > 0, R(2\mu-\lambda) < 3/2, R(p) > 0,$$

$\mu$  is not an integer or zero. When  $p = 0$ , then  $R(\mu) > 0$ ,  $R(2\mu-\lambda) < 3/2$ .

As a particular case, when  $\beta = \gamma$ , (17) yields a known integral.<sup>15</sup>

*Example 5.*—Taking

$$\begin{aligned}
 g(x) &= x^{\alpha-1} {}_2F_1(a, b; c; -1/x) \\
 &\doteq \Gamma(\alpha) p^{1-\alpha} {}_2F_2(a, b; c, 1-\alpha; p)
 \end{aligned}$$

<sup>15</sup> Watson, (15), p. 434.

$$\begin{aligned}
& + \frac{\Gamma(a+a)\Gamma(b+a)\Gamma(-a)\Gamma(c)}{\Gamma(a)\Gamma(b)\Gamma(c+a)} p \\
& \quad \times {}_2F_2(a+a, b+a; c+a, 1+a; p) \\
& = p^{2-l} h(p), \quad R(a+a) > 0, \quad R(b+a) > 0, \quad a \text{ is not an integer} \\
& \quad \text{or zero,}
\end{aligned}$$

we have

$$\begin{aligned}
h(x) &= \Gamma(a) x^{l-a-1} {}_2F_2(a, b; c, 1-a; x) \\
& + \frac{\Gamma(a+a)\Gamma(b+a)\Gamma(-a)\Gamma(c)}{\Gamma(a)\Gamma(b)\Gamma(c+a)} \\
& \quad \times x^{l-1} {}_2F_2(a+a, b+a; c+a, 1+a; x) \\
& \quad \times \frac{v}{v} \frac{\Gamma(l-a)\Gamma(l-a+2m)\Gamma(a)}{\Gamma(l-a+m-k+\frac{1}{2})} p^{a-l+1} \\
& \times {}_4F_3(a, b, l-a, l-a+2m; c, 1-a, l-a+m-k+\frac{1}{2}; 1/p) \\
& + \frac{\Gamma(l)\Gamma(l+2m)\Gamma(a+a)\Gamma(b+a)\Gamma(-a)\Gamma(c)}{\Gamma(a)\Gamma(b)\Gamma(c+a)\Gamma(l+m-k+\frac{1}{2})} p^{1-l} \\
& \quad \times {}_4F_3(a+a, b+a, l, l+2m; c+a, 1+a, l+m-k \\
& \quad \quad \quad + \frac{1}{2}; 1/p) \\
& = f(p), \quad R(l) > 0, \quad R(l+2m) > 0, \quad R(l-a), \quad R(l-a+2m) > 0, \\
& \quad \quad \quad R(p) > 0.
\end{aligned}$$

Hence the theorem gives with  $l = \lambda$ ,  $l + 2m = \mu$ ,  $l + m - k + \frac{1}{2} = \nu$ ,  $z = 1/p$

$$\begin{aligned}
& \int_0^\infty t^{a-1} {}_2F_1(\lambda, \mu; \nu; -tz) {}_2F_1(a, b; c; -1/t) dt \\
& = \frac{\Gamma(\lambda-a)\Gamma(\mu-a)\Gamma(a)\Gamma(\nu)}{\Gamma(\lambda)\Gamma(\mu)\Gamma(\nu-a)} z^{-a} \\
& \quad \times {}_4F_3(a, b, \lambda-a, \mu-a; c, 1-a, \nu-a; z) \\
& + \frac{\Gamma(a+a)\Gamma(b+a)\Gamma(-a)\Gamma(c)}{\Gamma(a)\Gamma(b)\Gamma(c+a)} \\
& \quad \times {}_4F_3(a+a, b+a, \lambda, \mu; c+a, 1+a, \nu; z), \quad (18)
\end{aligned}$$

valid by analytic continuation, for  $R(\lambda - a) > 0$ ,  $R(\mu - a) > 0$ ,  
 $R(a + a) > 0$ ,  $R(b + a) > 0$ ,  $R(z) > 0$ ,  $a$  not an integer or zero; if  
 $z = 0$ , then  $R(a + a) > 0$ ,  $R(b + a) > 0$ ,  $R(a) < 0$ .

As a special case of (18) take  $a = \frac{1}{2}$ ,  $\lambda = a$ ,  $\mu = b$ ,  $\nu = c$ . Since

$$\begin{aligned} & {}_4F_3\left(a, a + \frac{1}{2}, b, b + \frac{1}{2}; \frac{1}{2}, c, c + \frac{1}{2}; v^2\right) \\ & + \frac{2abv}{c} {}_4F_3\left(a + \frac{1}{2}, a + 1, b + \frac{1}{2}, b + 1; \frac{3}{2}, c + \frac{1}{2}, c + 1; v^2\right) \\ & = {}_2F_1(2a, 2b; 2c; v), \end{aligned}$$

we get<sup>16</sup> after a little simplification

$$\begin{aligned} & \int_0^\infty {}_2F_1(a, b; c; -tz) {}_2F_1(a, b; c; -1/t) \frac{dt}{\sqrt{t}} \\ & = \frac{\Gamma(a - \frac{1}{2}) \Gamma(b - \frac{1}{2}) \Gamma(c)}{\Gamma(a) \Gamma(b) \Gamma(c - \frac{1}{2})} \sqrt{\frac{\pi}{z}} {}_2F_1(2a-1, 2b-1; 2c-1; -\sqrt{z}), \end{aligned}$$

$R(a) > \frac{1}{2}$ ,  $R(b) > \frac{1}{2}$ ,  $R(z) > 0$ .

5. In this section we give another theorem for this transform.

THEOREM II.—If

$$f(p) \doteq h(x) \text{ and } p^{2-l} h(p) \frac{v}{v} g(x),$$

then

$$\begin{aligned} f(p) &= \frac{\Gamma(l) \Gamma(l + 2m)}{\Gamma(l + m - k + \frac{1}{2})} p \\ &\times \int_0^\infty t^{-l} {}_2F_1(l, l + 2m; l + m - k + \frac{1}{2}; -p/t) g(t) dt, \end{aligned}$$

provided that  $R(l) > 0$ ,  $R(l + 2m) > 0$ ,  $R(p) > 0$ ,  $R(\mu) > -1$ ,

$R(\mu + 2m) > 1$ ,  $R(l - \nu) > 1$ , when  $g(t) = 0(t^\mu)$  for small  $t$  and  $g(t) = 0(t^\nu)$  for large  $t$ .

The proof is similar to that of Theorem I.

<sup>16</sup> B. vander Pol and Bremmer (10), p. 249.

6. We consider below a few examples of this theorem.

*Example 1.*—Take (I.2)

$$g(x) = x^{c-2m-1} {}_3F_2\left(\frac{1}{2} - \lambda + \mu, \frac{1}{2} - \lambda - \mu, \frac{1}{2} + c - k - m; c, c - 2m; -x\right)$$

$$\stackrel{v}{=} \frac{\Gamma(c) \Gamma(c - 2m)}{\Gamma(\frac{1}{2} + c - k - m)} p^{2m-c-\lambda+1} e^{\frac{1}{2}p} W_{\lambda, \mu}(p)$$

$$= p^{2-l} h(p), \quad R(c) > 0, \quad R(c - 2m) > 0, \quad R(p) > 0.$$

Therefore

$$h(x) = \frac{\Gamma(c) \Gamma(c - 2m)}{\Gamma(\frac{1}{2} + c - k - m)} x^{l+2m-c-\lambda-1} e^{\frac{1}{2}x} W_{\lambda, \mu}(x)$$

$$\doteq \frac{\Gamma(c) \Gamma(c - 2m) \Gamma(A + \mu + 3/2) \Gamma(A - \mu + 3/2)}{\Gamma(\frac{1}{2} + c - k - m) \Gamma(A - \lambda + 2)} p$$

$$\times {}_2F_1(A + \mu + 3/2, A - \mu + 3/2; A - \lambda + 2; 1 - p)$$

$$= f(p), \quad R(A \pm \mu + 3/2) > 0, \quad A \equiv 2m + l - c - \lambda - 1.$$

Hence the theorem gives after replacing  $l$  by  $a$ ,  $l + 2m$  by  $\beta$ ,  $l + m - k + \frac{1}{2}$  by  $\gamma$ ,  $\frac{1}{2} - \lambda + \mu$  by  $a$ ,  $\frac{1}{2} - \lambda - \mu$  by  $b$  and  $c - l - 2m$  by  $\delta$ ,

$$\frac{\Gamma(a) \Gamma(\beta)}{\Gamma(\gamma)} \int_0^\infty t^{\delta-1} {}_3F_2(a, b, \delta + \gamma; \delta + a, \delta + \beta; -t)$$

$$\times {}_2F_1(a, \beta; \gamma; -p/t) dt$$

$$= \frac{\Gamma(\delta + a) \Gamma(\delta + \beta) \Gamma(a - \delta) \Gamma(b - \delta)}{\Gamma(\delta + \gamma) \Gamma(a + b - \delta)}$$

$$\times {}_2F_1(a - \delta, b - \delta; a + b - \delta; 1 - p), \quad (19)$$

valid by analytic continuation for  $R(\delta + a) > 0$ ,  $R(\delta + \beta) > 0$ ,

$R(a - \delta) > 0$ ,  $R(b - \delta) > 0$ ,  $R(\gamma) > 0$ ,  $R(p) > 0$ . When  $p = 0$ , we must have  $R(a - \delta) > 0$ ,  $R(b - \delta) > 0$ ,  $R(\delta) > 0$ ,  $R(\gamma) > 0$ .

*Example 2.*—Starting with

$$h(x) = x^{a-1} {}_2F_1(a, b; c; -1/x)$$

$$\doteq \Gamma(a) p^{1-a} {}_2F_2(a, b; c, 1 - a; p)$$

$$+ \frac{\Gamma(a+a)\Gamma(b+a)\Gamma(c)\Gamma(-a)}{\Gamma(a)\Gamma(b)\Gamma(c+a)} p$$

$$\times {}_2F_2(a+a, b+a; c+a, 1+a; p)$$

$$= f(p), R(a+a) > 0, R(b+a) > 0, R(p) > 0, a \text{ is not integral or } 0.$$

we have

$$p^{2-l} h(p) = p^{a-l+1} {}_2F_1(a, b; c; -1/p)$$

$$\frac{v}{v} \frac{\Gamma(l-a+m-k+\frac{1}{2})}{\Gamma(l-a)\Gamma(l-a+2m)} x^{l-a-1}$$

$$\times {}_3F_3(a, b, l-a+m-k+\frac{1}{2}; c, l-a, l-a+2m; -x)$$

$$= g(x), R(l-a) > 0, R(l-a+2m) > 0,$$

on backward interpretation by (I.5).

Writing  $\lambda$  for  $l$ ,  $\mu$  for  $l+2m$ ,  $\nu$  for  $l+m-k+\frac{1}{2}$  and applying the theorem we get

$$\begin{aligned} & \frac{\Gamma(\lambda)\Gamma(\mu)\Gamma(\nu-a)}{\Gamma(\lambda-a)\Gamma(\mu-a)\Gamma(\nu)} \int_0^\infty t^{-a-1} {}_2F_1(\lambda, \mu; \nu; -p/t) \\ & \times {}_3F_3(a, b, \nu-a; c, \lambda-a, \mu-a; -t) dt \\ & = \Gamma(a) p^{-a} {}_2F_2(a, b; c, 1-a; p) + \frac{\Gamma(a+a)\Gamma(b+a)\Gamma(c)\Gamma(-a)}{\Gamma(a)\Gamma(b)\Gamma(c+a)} \\ & \times {}_2F_2(a+a, b+a; c+a, 1+a; p), \end{aligned} \quad (20)$$

valid by analytic continuation, for  $R(\lambda-a) > 0$ ,  $R(\mu-a) > 0$ ,

$R(a+a) > 0$ ,  $R(b+a) > 0$ ,  $R(\nu) > 0$ ,  $R(p) > 0$ ,  $a$  non-integral and non-zero. If  $p=0$ , then  $R(a) < 0$ ,  $R(a+a) > 0$ ,  $R(b+a) > 0$ ,  $R(\nu) > 0$ .

Some special cases of (20) are worth mentioning.

(i) Taking in (20),  $b=c$  and replacing  $a$  by  $2m$  and  $a$  by  $\frac{1}{2}-k-m$ , we get

$$\begin{aligned} & \frac{\Gamma(\lambda)\Gamma(\mu)\Gamma(\nu-2m)}{\Gamma(\lambda-2m)\Gamma(\mu-2m)\Gamma(\nu)} \int_0^\infty t^{-2m-1} {}_2F_1(\lambda, \mu; \nu; -p/t) \\ & \times {}_2F_2(\frac{1}{2}-k-m, \nu-2m; \lambda-2m, \mu-2m; -t) dt \end{aligned}$$

$$\begin{aligned}
&= \Gamma(2m) p^{-2m} {}_1F_1\left(\frac{1}{2} - k - m; 1 - 2m; p\right) \\
&\quad + \frac{\Gamma\left(\frac{1}{2} - k + m\right) \Gamma(-2m)}{\Gamma\left(\frac{1}{2} - k - m\right)} \\
&\quad \times {}_1F_1\left(\frac{1}{2} - k + m; 1 + 2m; p\right) \\
&= \Gamma\left(\frac{1}{2} + m - k\right) p^{-m-\frac{1}{2}} e^{\frac{1}{2}p} W_{k,m}(p),
\end{aligned}$$

on using a well-known result.<sup>17</sup>

Thus we have another integral representation for Whittaker function

$$\begin{aligned}
W_{k,m}(p) &= \frac{\Gamma(\lambda) \Gamma(\mu) \Gamma(\nu - 2m) e^{-\frac{1}{2}p} p^{m+\frac{1}{2}}}{\Gamma(\lambda - 2m) \Gamma(\mu - 2m) \Gamma(\nu) \Gamma\left(\frac{1}{2} + m - k\right)} \\
&\quad \times \int_0^\infty t^{-2m-1} {}_2F_1(\lambda, \mu; \nu; -p/t) {}_2F_2\left(\frac{1}{2} - k - m, \nu - 2m; \lambda - 2m, \right. \\
&\quad \left. \mu - 2m; -t\right) dt, \tag{21}
\end{aligned}$$

valid for  $R(p) > 0$ ,  $R(\lambda - 2m) > 0$ ,  $R(\mu - 2m) > 0$ ,  $R(\nu) > 0$ ,  
 $R\left(\frac{1}{2} + m - k\right) > 0$ .

Further, if we put  $\lambda = \frac{1}{2} - k + m$  in (21), we have

$$\begin{aligned}
W_{k,m}(p) &= \frac{\Gamma(\mu) \Gamma(\nu - 2m) e^{-\frac{1}{2}p} p^{m+\frac{1}{2}}}{\Gamma\left(\frac{1}{2} - m - k\right) \Gamma(\mu - 2m) \Gamma(\nu)} \\
&\quad \times \int_0^\infty t^{-2m-1} {}_2F_1\left(\frac{1}{2} - k + m, \mu; \nu; -p/t\right) {}_1F_1(\nu - 2m; \\
&\quad \mu - 2m; -t) dt \tag{22}
\end{aligned}$$

$R\left(\frac{1}{2} - m - k\right) > 0$ ,  $R(\mu - 2m) > 0$ ,  $R(\nu) > 0$ ,  $R(p) > 0$ .

In (21) take  $m = \frac{1}{2}$  and replace  $k$  by  $n$ . Since

$$W_{n, \frac{1}{2}}(x) = \Gamma(n+1) k_{2n}(x/2)$$

where  $k_{2n}(x)$  is Bateman's function, we get

$$\begin{aligned}
k_{2n}\left(\frac{1}{2}p\right) &= \frac{(\lambda - 1)(\mu - 1) e^{\frac{1}{2}p} p}{(\nu - 1) n\pi \operatorname{cosec} n\pi} \int_0^\infty t^{-2} {}_2F_1(\lambda, \mu; \nu; -p/t) \\
&\quad \times {}_2F_2(-n, \nu - 1; \lambda - 1, \mu - 1; -t) dt,
\end{aligned}$$

$R(\lambda) > 1$ ,  $R(\mu) > 1$ ,  $R(n) < 1$ ,  $R(\nu) > 0$ ,  $R(p) > 0$ .

<sup>17</sup> M. A., p. 346.

Similarly by giving to  $k$  and  $m$  suitable values one may write the corresponding integrals for various functions such as  $K_\nu(x)$ ,  $D_\nu(x)$ . Moreover by making proper choice of  $\mu$  and  $\nu$  several particular cases of these integrals can be obtained.

When  $\mu = \nu$ , (22) yields Whittaker's integral,<sup>18</sup> while with  $\nu = \frac{1}{2} - k + m$  it gives a result due to Hari Shanker.<sup>19</sup>

(ii) Denoting the right side of equation (20) by  $P$  we easily deduce that

$$\int_0^\infty t^{\lambda-a-1} (p+t)^{-\lambda} {}_2F_2(a, b; c, \lambda-a; -t) dt = \frac{\Gamma(\lambda-a)}{\Gamma(\lambda)} P,$$

$R(\lambda-a) > 0$ ,  $R(a+a) > 0$ ,  $R(b+a) > 0$ ,  $R(p) > 0$ ,  $a$  non-integral and non-zero.

$$\begin{aligned} \int_0^\infty t^{-a-1} {}_2F_1(a+a, \mu; \nu; -p/t) {}_2F_2(b, \nu-a; c, \mu-a; -t) dt \\ = \frac{\Gamma(a) \Gamma(\mu-a) \Gamma(\nu)}{\Gamma(a+a) \Gamma(\mu) \Gamma(\nu-a)} P, \end{aligned}$$

$R(a) > 0$ ,  $R(b+a) > 0$ ,  $R(\mu-a) > 0$ ,  $R(\nu) > 0$ ,  $R(p) > 0$ ,  $a$  non-integral and non-zero,

$$\begin{aligned} \int_0^\infty t^{-a-1} {}_2F_1(a+a, b+a; \nu; -p/t) {}_1F_1(\nu-a; c; -t) dt \\ = \frac{\Gamma(a) \Gamma(b) \Gamma(\nu)}{\Gamma(a+a) \Gamma(b+a) \Gamma(\nu-a)} P, \end{aligned}$$

$R(a) > 0$ ,  $R(b) > 0$ ,  $R(\nu) > 0$ ,  $R(p) > 0$ ,  $a$  non-integral and non-zero.

*Example 3.*—Take

$$g(x) = x^{a-1} {}_2F_3(b, a+m-k+\frac{1}{2}; a, a+2m, c; -x)$$

$$\frac{v}{v} \frac{\Gamma(a) \Gamma(a+2m)}{\Gamma(a+m-k+\frac{1}{2})} p^{1-a} {}_1F_1(b; c; -1/p)$$

$$= p^{2-l} h(p), R(a) > 0, R(a+2m) > 0, R(p) > 0,$$

<sup>18</sup> M. A., p. 340.

<sup>19</sup> Hari Shanker, (6).



so that

$$\begin{aligned}
 h(x) &= \frac{\Gamma(a) \Gamma(a+2m)}{\Gamma(a+m-k+\frac{1}{2})} x^{l-a-1} {}_1F_1(b; c; -1/x) \\
 &\doteq \frac{\Gamma(a) \Gamma(a+2m)}{\Gamma(a+m-k+\frac{1}{2})} [ \Gamma(l-a) p^{a-l+1} {}_1F_2(b; 1+a-l, c; p) \\
 &\quad + \frac{\Gamma(c) \Gamma(b+l-a) \Gamma(a-l)}{\Gamma(b) \Gamma(c+l-a)} p \\
 &\quad \times {}_1F_2(b+l-a; 1-a+l, c+l-a; p) ] \\
 &= f(p), \quad R(b+l-a) > 0, \quad a-l \text{ non-integral and non-zero.}
 \end{aligned}$$

Hence replacing  $l$  by  $\lambda$ ,  $l+2m$  by  $\mu$ , and  $l+m-k+\frac{1}{2}$  by  $\nu$  we get from the theorem

$$\begin{aligned}
 &\frac{\Gamma(\lambda) \Gamma(\mu)}{\Gamma(\nu)} \int_0^\infty t^{a-\lambda-1} {}_2F_1(\lambda, \mu; \nu; -p/t) {}_2F_2(b, a+\nu-\lambda; \\
 &\quad a, a+\mu-\lambda, c; -t) dt \\
 &= \frac{\Gamma(a) \Gamma(a+\mu-\lambda)}{\Gamma(a+\nu-\lambda)} [ \Gamma(\lambda-a) p^{a-\lambda} {}_1F_2(b; 1+a-\lambda, c; p) \\
 &\quad + \frac{\Gamma(c) \Gamma(b+\lambda-a) \Gamma(a-\lambda)}{\Gamma(b) \Gamma(c+\lambda-a)} \times \\
 &\quad \times {}_1F_2(b+\lambda-a; 1-a+\lambda, c+\lambda-a; p) ], \quad (23)
 \end{aligned}$$

valid by analytic continuation for  $R(a) > 0$ ,  $R(a+\mu-\lambda) > 0$ ,

$R(a+b+\nu-2\lambda-\mu-c) < \frac{1}{2}$ ,  $R(p) > 0$ ,  $a-l$  non-integral and non-zero.

A few special cases of (23) may be noted.

(i) Putting  $b=c$ , we get

$$\begin{aligned}
 &\int_0^\infty t^{a-\lambda-1} {}_2F_1(\lambda, \mu; \nu; -p/t) {}_1F_2(a+\nu-\lambda; a, a+\mu-\lambda; -t) dt \\
 &= \frac{\Gamma(a) \Gamma(\nu) \Gamma(a+\mu-\lambda)}{\Gamma(\lambda) \Gamma(\mu) \Gamma(a+\nu-\lambda)} 2p^{\frac{1}{2}(a-\lambda)} K_{a-\lambda}(2\sqrt{p}), \quad (24)
 \end{aligned}$$

$R(a) > 0$ ,  $R(a+\mu-\lambda) > 0$ ,  $R(a+\nu-2\lambda-\mu) < \frac{1}{2}$ ,  $R(p) > 0$ .

If in (24) we take  $a=3/2$ ,  $\mu=\chi+\lambda$ ,  $\nu=\lambda-\frac{1}{2}$  and use

$$H_x(2\sqrt{t}) = \frac{t^{\frac{1}{2}(\chi+1)}}{\Gamma(3/2) \Gamma(3/2+\chi)} {}_1F_2(1; 3/2, 3/2+\chi; -t)$$

where  $H_x$  is Struve's function, we have

$$\begin{aligned} & \int_0^\infty t^{-\lambda-\frac{1}{2}x} {}_2F_1(\lambda, \chi + \lambda; \lambda - \frac{1}{2}; -p/t) H_x(2\sqrt{t}) dt \\ &= \frac{\Gamma(\lambda - \frac{1}{2})}{\Gamma(\lambda) \Gamma(\chi + \lambda)} 2p^{\frac{1}{2}-\lambda} K_{2,2-\lambda}(2\sqrt{p}). \end{aligned}$$

$R(\chi) > -3/2$ ,  $R(\lambda) > \frac{1}{2}$ , such that  $R(2\lambda + \chi) > \frac{1}{2}$ ,  $R(p) > 0$ .

On the other hand if we take  $a = \nu + 1$ ,  $\lambda = \nu + \frac{1}{2}$ ,  $\mu = 2\nu + \frac{1}{2}$ , we get

$$\begin{aligned} & \int_0^\infty {}_2F_1(\nu + \frac{1}{2}, 2\nu + \frac{1}{2}; \nu; -p/t) J_\nu^2(\sqrt{t}) \frac{dt}{\sqrt{t}} \\ &= \frac{\Gamma(\nu)}{\Gamma(\nu + \frac{1}{2}) \Gamma(2\nu + \frac{1}{2})} e^{-2\sqrt{p}} \end{aligned}$$

$R(\nu) > 0$ ,  $R(p) > 0$ .

(ii) With  $\mu = \nu$  and  $b = a$  (23) yields a known integral (B.F., p. 434).

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# ON CERTAIN DIRICHLET'S SERIES—II

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1. In a combined paper, we have proved that the following Dirichlet series represent integral functions as their sum functions:

$$(1.1) \quad \sum_{n=1}^{\infty} e^{Aif(n) - s\lambda_n} \quad 0 < A \leq 2\pi.$$

$$(1.2) \quad \sum_{n=1}^{\infty} e^{Aif(n)} \phi(n) e^{-s\lambda_n} \quad 0 < A \leq 2\pi$$

where the functions  $f(z)$ ,  $\phi(z)$  and  $\lambda(z)$  satisfy certain properties given in that paper.<sup>1</sup>

In this paper, I wish to prove the following theorem:—

2. THEOREM:—

$$(2.1) \quad \text{Suppose } F(s) = \sum_{n=1}^{\infty} \phi(n) e^{-s\lambda_n \log n} \quad (s) = \sigma + it$$

$p$  being a positive integer greater than one. Let  $\phi(z)$  satisfy the following conditions:—

$$(2.12) \quad \phi(z) \text{ is an analytic function of } z (= \beta + \rho e^{i\psi}, \beta < p) \text{ in the half plane } R(z) \geq \beta;$$

$$(2.13) \quad \lim_{p \rightarrow \infty} \sup \left\{ \frac{\log |\phi(\beta + \rho e^{i\psi})|}{\rho} \right\} \log \rho = \lambda(\psi).$$

where  $\lambda(\psi)$  is continuous for  $|\psi| \leq \frac{\pi}{2}$  and  $\leq k < \pi$ , for  $|\psi| \leq \frac{\pi}{2}$

Then  $F(s)$  is an analytic function of  $S$  in a region lying outside a certain curve  $\Sigma$ , which is only  $\Gamma$ , the associated curve of  $\phi$ , displaced in a particular manner, and which has tangents at its extremities added to it, in case it be finite.

Let  $\lambda(0) = k$ , then  $k_1 \leq k$ , and the Dirichlet's series is absolutely and uniformly convergent in the region lying  $\sigma \geq k_1 + \delta > k_1$ .

Now with centre  $\beta$ , and radius  $R = n + \frac{1}{2} - \beta$ , describe the semi-circle  $PCQ$ .

Then by Cauchy's theorem

$$\sum_p^{\infty} \phi(p) e^{-s p / \log p} = \int_S \frac{\phi(z) e^{-s z / \log z}}{e^{2\pi i z} - 1} dz$$

where  $S$  is the contour  $\beta P c Q$ .

$$(2.14) \quad \text{Now } \left| \frac{1}{e^{2\pi i z} - 1} \right| = 0 \quad (e^{-2\pi \rho |\sin \psi|}) \text{ over the arc } PC; \text{ i.e., } -\frac{\pi}{2} \leq \psi < 0.$$

$$(2.15) \quad \text{and } \left| \frac{1}{e^{2\pi i z} - 1} \right| = 0 \quad (1) \text{ over the arc } CQ \text{ for } 0 \leq \psi \leq \frac{\pi}{2}.$$

$$(2.16) \quad \text{Also } \left| \frac{1}{e^{-2\pi i z} - 1} \right| = 0 \quad (e^{-2\pi \rho |\sin \psi|}) \text{ over the arc } CQ.$$

The modulus of the integrand over the arc  $PC$  (putting  $z = \beta + \rho e^{i\psi}$ ) is

$$(2.2) \quad 0 \left( \rho e^{\frac{k\rho}{\log \rho} - \frac{\rho}{\log \rho} (\sigma \cos \psi - t \sin \psi) - 2\pi \rho |\sin \psi|} \right)$$

which  $\rightarrow 0$  as  $\rho \rightarrow \infty$ , due to the predominant factor  $e^{-2\pi \rho |\sin \psi|}$ ,  $\psi$  varying from  $-\frac{\pi}{2}$  to 0.

Similarly the integral over the arc  $CQ \rightarrow 0$  as  $\rho \rightarrow \infty$ , if  $S$  lies in the region

$$\sigma \cos \psi - t \sin \psi \geq k + \delta > k > \lambda(\psi).$$

Hence if  $\sigma > k$  and bounded, the integral over the arc  $PCQ \rightarrow 0$  as  $\rho \rightarrow \infty$ , and we have the equation

$$(2.3) \quad F(s) = \sum_p^{\infty} \phi(p) e^{-s p / \log p} = \int_{\beta}^{\infty} \frac{\phi(z) e^{-s z / \log z}}{e^{2\pi i z} - 1} dz - \int_{\beta}^{\infty} \frac{\phi(z) e^{-s z / \log z}}{e^{2\pi i z} - 1} dz \\ = \int_{\beta}^{\infty} \phi(x) e^{-s x / \log x} dx + \int_{\beta}^{\infty} \frac{\phi(z) e^{-s z / \log z}}{e^{-2\pi i z} - 1} dz + \int_{\beta}^{\infty} \frac{\phi(z) e^{-s z / \log z}}{e^{2\pi i z} - 1} dz.$$

The right side giving the analytic continuation of the function represented by the Dirichlet's series in the region  $\sigma \geq k_1 + \delta$ .

Now we wish to show that each of the last two integrals represents an analytic function of  $s$  in any finite part of the plane.

The integral  $\int_{\beta}^{\infty} \frac{\phi(z) e^{-sz|\log z|}}{e^{2\pi iz} - 1} dz$  is absolutely and uniformly convergent

over the entire plane of  $s$ ,  $\sigma$  being bounded.

Similarly the integral

$$\int_{\beta}^{\infty (\pi/2)} \frac{\phi(z) e^{-sz|\log z|}}{e^{-2\pi iz} - 1} dz$$

is absolutely and uniformly convergent over the region  $\sigma \cos \psi - t \sin \psi \geq k + \delta > k > \lambda(\psi)$ .

Hence both these integrals represent an analytic function of  $s$  in the region

$$\sigma \cos \psi - t \sin \psi > k = \lambda(\psi).$$

and we denote their sum by  $g(s)$ .

$\therefore$  equation (2.3) becomes

$$(2.4) \quad F(s) = g(s) + \int_{\beta}^{\infty} \phi(z) e^{-sz|\log z|} dz = g(s) + J(s).$$

Now arguing with the integral on the right side of (2.4), we have

$\dagger J(s) = \int_{\beta}^{\infty (\psi)} \phi(z) e^{-sz|\log z|} dz$ , where  $\psi$  may have any value whatever in the range  $-\pi/2 \leq \psi \leq \pi/2$  so that  $J(s)$  is an analytic function of  $s$ , outside the envelope of the lines

$$(2.5) \quad \sigma \cos \psi - t \sin \psi = \lambda(\psi),$$

where  $\psi$  moves continuously from  $-\pi/2$  to  $\pi/2$  and  $\lambda(\psi)$  is continuous for  $|\psi| \leq \pi/2$  and  $\leq k$  for  $|\psi| \leq \pi/2$ .

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$$\dagger \left| i \int_{\beta}^{\theta} \phi(\rho e^{i\psi}) e^{-\delta \rho e^{i\psi}} / \log(\rho e^{i\psi}) d\psi \right| \rightarrow 0 \text{ as } \rho \rightarrow \infty \text{ as } \left[ \phi(\rho e^{i\psi}) e^{-\delta \rho e^{i\psi}} / \log(\rho e^{i\psi}) d\psi \right] \\ = 0 \{ e^{-\rho/\log \rho} (\sigma \cos \psi - t \sin \psi - \lambda(\psi)) \} \text{ which } \rightarrow 0 \text{ if } \sigma \cos \psi - t \sin \psi \geq \lambda(\psi). ]$$

Now,  $\Gamma$ ,  $p = \lambda(\psi)$ ,  $|\psi| \leq \pi/2$ , the associated curve of  $\phi$ , is defined as the envelope of its tangents, which exist for every value of  $\psi$  between  $-\pi/2$  and  $\pi/2$ . Choose a particular value of  $\psi$  say  $\psi_1$  and consider the corresponding tangent to  $\Gamma$ . Superimpose the  $\Gamma$  over the  $s$ -plane, the origins and the axes coinciding. Turn the tangent  $\psi_1$  to  $\Gamma$  through a right angle in the negative direction in its own plane, and then turn it through an angle  $\pi$ , round the vertical line through the origin, then its tangent will come to coincide with the line

$$\sigma \cos \psi - t \sin \psi_1 = \lambda(\psi_1)$$

in the  $s$ -plane.

Hence  $\Sigma$ , the envelope of the lines (2.5) is the curve  $\Gamma$  displaced in a manner indicated above for the tangent  $\psi_1$ .

Now  $\Sigma$  being obtained as the envelope of its tangents, it is clear that it must have tangents at its extremities, added to its curved portion, unless the curved portion extends to infinity.

This completes the proof of the theorem given at the beginning of Section 2.

3. As a particular case if

$$\lambda(\psi) = A \cos \psi + B \sin \psi.$$

(2.5) becomes

$$\sigma \cos \psi - t \sin \psi = A \cos \psi + B \sin \psi + \epsilon.$$

Now its envelope is

$$(3.1) \quad (\sigma - A)^2 + (t + B)^2 = \epsilon^2$$

so that it follows that  $F(S)$  is a regular function of  $S$  in the whole plane except at the point  $A - iB$ .

I am indebted to Dr. P. L. Srivastava, under whose guidance I have obtained these results.

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# THE TEMPERATURE DEPENDENCE OF VISCOSITY OF NON-POLAR GASES

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## INTRODUCTION

The basic theory of the transport properties of gases was developed by Chapman, Enskog and others and the transport coefficients have been expressed in terms of a set of collision integrals  $\Omega_k^j$  by Chapman and Cowling (1939). The actual evaluation of these integrals was however done only for a few simple molecular models such as the repulsive inverse power model (with Maxwellian molecules, and rigid, elastic, smooth and spherical molecules as its particular cases), the Sutherland model, etc., which are all unrealistic. The various Lennard-Jones models and specially the 12:6 model has been found to be more in accord with the observed properties of gases, and recently Hirschfelder, Bird and Spotz (1948) have evaluated the collision integrals for this 12:6 model. Using these values, the transport properties for certain gases and gas mixtures have been calculated and compared with the experimental data by Hirschfelder *et al.* (1948, 1949), Winter (1950), Davenport and Winter (1951) and others. They have however assumed the intermolecular force constant to be absolutely invariable, but it has been shown by the present authors (1953), from a study of the thermal diffusion data of argon, that the intermolecular force constant is found to vary with temperature. It is the purpose of the present paper to examine critically the existing data on the viscosity of a few simple non-polar gases to discover if they also exhibit any variation in the value of the intermolecular force constant  $\epsilon$ .

According to the 12:6 model, the potential energy of molecular interaction for non-polar gases is given by

$$E(r) = 4\epsilon \left[ \left( \frac{r_0}{r} \right)^{12} - \left( \frac{r_0}{r} \right)^6 \right], \quad (1)$$

where  $r_0$  is the separation for which the energy of interaction is zero (collision diameter for low-velocity head-on collisions) and  $\epsilon$  is the numerical value of the maximum negative energy. From Chapman-Enskog theory

the coefficient of viscosity  $\eta$  of a pure component, as shown by Hirschfelder *et al.* (1948), can be written in the form

$$\eta = (5/8r_0^2) \left( \frac{\mu kT}{2\pi} \right)^{\frac{1}{2}} (V/W_2^{(2)}), \quad (2)$$

where  $V$  is given by

$$V = \left[ 1 + \frac{b_{12}^2}{(b_{11}b_{22} - b_{12}^2)} + \frac{b_{11}(b_{12}b_{23} - b_{22}b_{12})^2}{(b_{11}b_{22} - b_{12}^2)(b_{11}b_{22}b_{33} + 2b_{12}b_{13}b_{23} - b_{12}^2b_{33} - b_{23}^2b_{11} - b_{13}^2b_{22})} + \dots \right]$$

$$b_{11}/Q = 4W_2^{(2)}$$

$$b_{12}/Q = 7W_2^{(2)} - W_3^{(2)}$$

$$b_{22}/Q = (301/12) W_2^{(2)} - 7W_3^{(2)} + W_4^{(2)}$$

$$b_{13}/Q = (63/8) W_2^{(2)} - (9/8) W_3^{(2)} + (1/2) W_4^{(2)}$$

$$b_{23}/Q = (1365/32) W_2^{(2)} - (321/16) W_3^{(2)} + (25/8) (1/4)$$

$$W_4^{(2)} - W_5^{(2)}$$

$$b_{33}/Q = (25137/256) W_2^{(2)} - (1755/32) W_3^{(2)} + (381/32)$$

$$W_4^{(2)} - (9/8) W_5^{(2)} + (1/16) W_6^{(2)} + (1/2) W_4^{(4)},$$

and

$$Q = r_0^2 \left( \frac{2\pi kT}{\mu} \right)^{\frac{1}{2}}; \quad \mu = \frac{m_1 m_2}{m_1 + m_2},$$

$m_1, m_2$  being the masses of the colliding molecules, and the various  $W$ 's are complicated functions of  $kT/\epsilon$ . The values of  $V/W_2^{(2)}$  have been tabulated by Hirschfelder *et al.* for different values of  $kT/\epsilon$ . Thus if  $\epsilon$  and  $r_0$  were known, say from the equation of state data, the viscosity of gases could be calculated theoretically. Actually, however, the experimental errors in the measurement of viscosity of gases by modern improved methods is so small, that the temperature dependence of viscosity provides a more accurate method for determining the intermolecular force constant, than that given by the second virial coefficient.

#### CALCULATION OF $\epsilon$ AND $r_0$

It is obvious from equation (2) that if the viscosity at two temperatures be known,  $\epsilon$  and  $r_0$  could be determined. Since, however, the explicit algebraic expressions for  $V$  and  $W_2^{(2)}$  in terms of  $kT/\epsilon$  are very much involved, the solution of the two equations for calculating  $\epsilon$  is a tedious affair and is therefore not considered worthwhile. We have consequently adopted a simpler graphical method, as explained below



First a graph of  $\eta/T^{\frac{1}{2}}$  against  $T$  was drawn (Fig. 1) to smoothen the data and to test their self-consistency. Now from equation (2) it follows that

$$\frac{[\eta/T^{\frac{1}{2}}]_2}{[\eta/T^{\frac{1}{2}}]_1} = \frac{[V/W_2^{(2)}]_2}{[V/W_2^{(2)}]_1}. \quad (3)$$

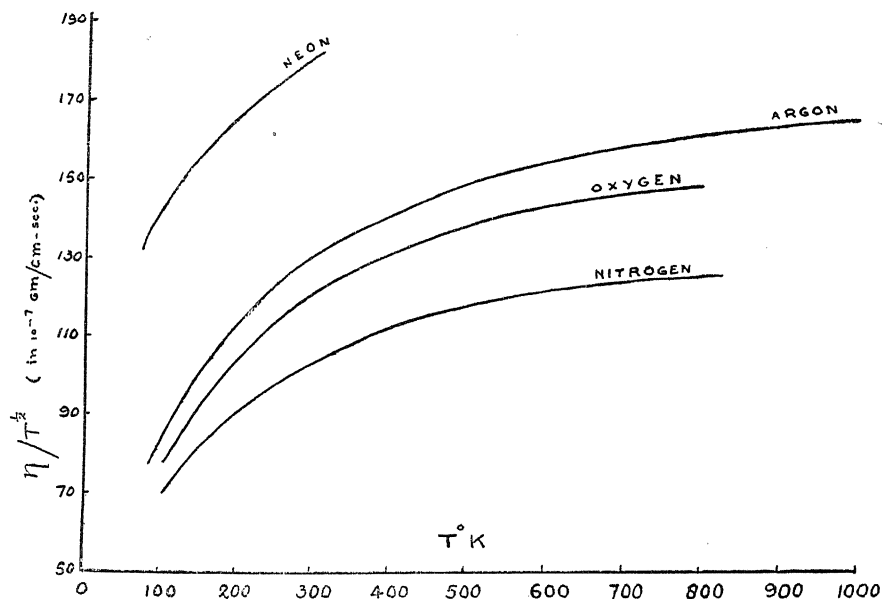


FIG. 1

Next  $V/W_2^{(2)}$  was plotted against  $kT/\epsilon$  (Fig. 2) and the values of  $[V/W_2^{(2)}]_2/[V/W_2^{(2)}]_1$  were calculated from this plot for various initial values of  $[V/W_2^{(2)}]_1$  for the  $[kT/\epsilon]_2/[kT/\epsilon]_1$  ratios equal to 2 and 2.5. These are

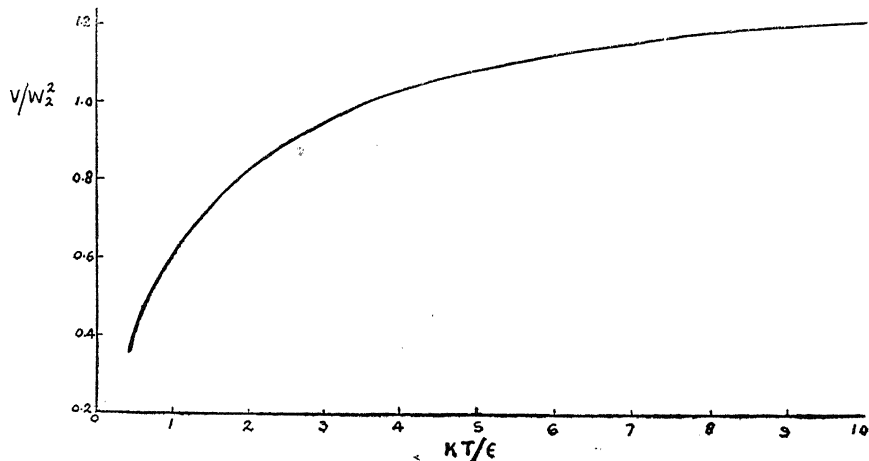


FIG. 2

plotted in Fig. 3 against the corresponding initial values of  $[V/W_2^{(2)}]_1$ . From the observed viscosity data plotted in Fig. 1, the ratio of the left-hand side of equation (3) was found for different initial temperatures  $T_1$  for the same

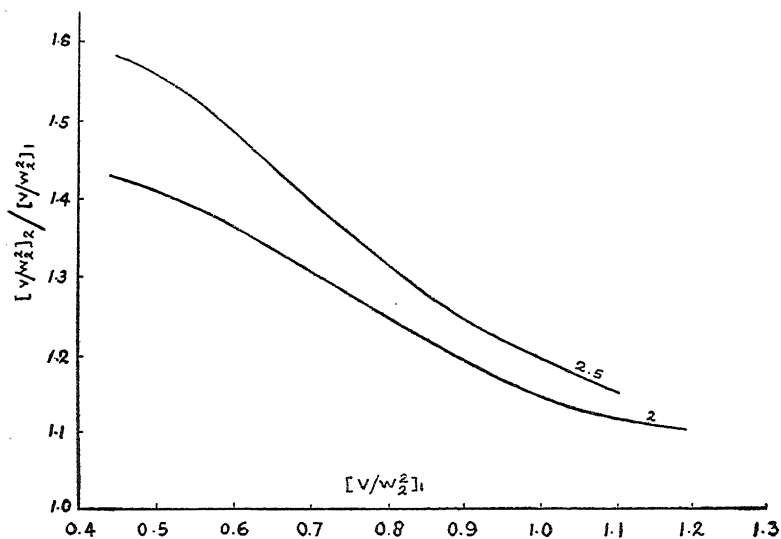


FIG. 3

$T$  or  $kT/\epsilon$  (since they are proportional if  $\epsilon$  is constant) ratios of 2 and 2.5, and the point representing the same value of the ordinate in Fig. 3, on the appropriate  $[V/W_2^{(2)}]_2/[V/W_2^{(2)}]_1$  ratio graph was noted and the corresponding abscissa read giving the value of  $[V/W_2^{(2)}]_1$  corresponding to  $T_1$ . Then from Fig. 2 the value of  $[kT/\epsilon]_1$  corresponding to this value of  $[V/W_2^{(2)}]_1$  was read. Knowing  $[kT/\epsilon]_1$  and  $T_1$ ,  $\epsilon$  was calculated.

This was done for various temperature intervals both in the low temperature and high temperature ranges for various gases. The results are given in Tables 1-4. The viscosity data utilized for these calculations are

TABLE I. Argon

Temp. Range ° K.	$\epsilon/k$	$r_0$ in Å.	Temp. Range ° K.	$\epsilon/k$	$r_0$ in Å.
100-250	104.2	3.533	200-400	127.7	3.407
105-262.5	109.5	3.509	225-450	125.0	3.422
110-275	113.9	3.464	250-500	127.2	3.411
120-300	116.5	3.453	300-600	125.0	3.414
130-260	115.8	3.454			
Mean	112.0	3.483	Mean	126.2	3.414

TABLE II. *Oxygen*

Temp. Range ° K.	$\epsilon/k$	$r_0$ in Å.	Temp. Range ° K.	$\epsilon/k$	$r_0$ in Å.
100-250	107.5	3.468			
110-220	116.5	3.406	200-400	131.8	3.328
110-275	113.4	3.434	225-450	135.1	3.316
115-287.5	111.2	3.443	250-500	136.3	3.320
120-300	111.1	3.449	300-600	136.3	3.335
140-280	116.6	3.407			
Mean	112.7	3.435	Mean	134.9	3.325

TABLE III. *Nitrogen*

Temp. Range ° K.	$\epsilon/k$	$r_0$ in Å.	Temp. Range ° K.	$\epsilon/k$	$r_0$ in Å.
100-250	85.76	3.716			
110-220	89.21	3.693	200-400	114.4	3.534
110-275	90.47	3.680	225-450	114.5	3.542
115-287.5	91.27	3.678	250-500	116.2	3.542
120-300	87.84	3.698	300-600	123.3	3.529
140-280	94.45	3.656			
Mean	89.8	3.687	Mean	117.1	3.537

TABLE IV. *Neon*

Temp. Range ° K.	$\epsilon/k$	$r_0$ in Å.
100-200	35.97	2.810
100-250	38.46	2.789
110-220	39.28	2.784
110-275	41.04	2.763
120-300	44.44	2.738
140-280	46.70	2.729
Mean	41.0	2.769

those listed by Hirschfelder *et al.* (1948). Values of  $\epsilon$  and  $r_0$  for the different ranges of temperatures were calculated and their average values for the low temperature range and for the high temperature range were separately found.

#### DISCUSSION OF RESULTS

It will be seen from the tables for argon, nitrogen and oxygen that the high temperature values of  $\epsilon$  are higher than the low temperature values, but the previous workers have assumed  $\epsilon$  to be constant throughout the range. This result of ours is, however, in agreement with our calculations from the thermal diffusion data. The reasons for the variation of  $\epsilon$  in the case of argon have already been discussed in detail in that paper, and the same would generally apply to nitrogen and oxygen also.

It must be remembered that the calculation of  $\epsilon$  from viscosity data essentially depends on the rate of variation of viscosity with temperature, and is based on the assumption that both  $\epsilon$  and  $r_0$  are constant. This will be profoundly modified if  $r_0$  varies with temperature. We see here that the values of  $\epsilon$  for nitrogen and oxygen in the high temperature range are respectively 117.1 and 134.9, and in the low temperature range 89.8 and 112.7. The low temperature values are in good agreement with those given by Hirschfelder *et al.* from viscosity and from virial coefficient data, but the high temperature values are higher. The magnitude of variation of  $\epsilon$  cannot be quantitatively discussed as the assumed constancy of  $r_0$  makes the calculation of  $\epsilon$  only a rough approximation.

In the case of argon, the values of  $\epsilon$  in the low and high temperature ranges are 112.0; and 126.2 respectively. From the thermal diffusion data also we found that  $\epsilon$  increases with temperature for argon, but the magnitude of variation observed here is somewhat smaller than that given by thermal diffusion. In view of the comparative insensitivity of viscosity to the value of  $\epsilon$  and the assumed constancy of  $r_0$  in the calculations, it is not worthwhile to discuss this difference quantitatively.

In the case of neon, the average value of  $\epsilon$  in the low temperature range is found to be 41.0, with values ranging from 36.0 to 46.7. The comparatively larger deviations in the value of  $\epsilon$  observed here seem to be significant when we remember that the 12.6 power law is unable to account for the large values of the thermal diffusion ratio observed at high temperatures.

It will be seen from Fig. 1 that the variation of  $\eta/T^{1/2}$  with temperature is less marked at higher temperatures than at low temperatures. In consequence, the values of  $\epsilon$ , as calculated from low temperature viscosity data,

will be relatively more accurate than those from high temperature data; nevertheless the increase in the value of  $\epsilon$  with increase of temperature seems to be definitely shown by the viscosity data.

The decrease of  $r_0$  with increase of temperature, of which we get definite indications from the present investigations, require more thorough investigation by properly pooling together all the transport properties and is elsewhere. From the viscosity data alone it is not possible to disentangle the effects of variation of  $\epsilon$  and of  $r_0$  from each other.

We record with pleasure our thanks to the Government of Uttar Pradesh for the award of a research grant which enabled the award of a research scholarship to one of us (M. P. M.).

#### SUMMARY

In this paper the Chapman-Enskog theory of the transport properties of gases has been utilized, in conjunction with the Lennard-Jones 12:6 power potential energy function for molecular interaction, to calculate the intermolecular force constant  $\epsilon$  and the low-velocity collision diameter  $r_0$  from the experimentally observed viscosities of gaseous argon, oxygen, nitrogen and neon at different temperatures. The values of the collision integrals given by Hirschfelder, Bird and Spotz for the 12:6 model have been used for this purpose. In contrast with the previous workers,  $\epsilon$  has been calculated for different ranges of temperature to discover, if it varies with temperature. It has been found that for argon, oxygen and nitrogen,  $\epsilon$  has a larger value at higher temperatures than at lower temperatures, in general agreement with the authors' investigations of the thermal diffusion of argon published elsewhere.

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## THEORY OF THE CLARINET

By R. G. CHATTERJI

THE clarinet is generally considered as acting as a closed pipe with its tone containing only odd harmonics. However, it is now well known that its tones contain even harmonics also, though very feeble. Some twelve years ago Ghosh<sup>1</sup> published a paper under the above heading basing his theory, to explain the presence of even harmonics, on the assumption of partial closure of the aperture under the reed. McGinnis and Gallagher<sup>2</sup> in their investigation of mode of vibration of reed found that their stroboscopic observation did not support the above assumption. However, by taking a continuous motion picture of vibration of a section of reed we have been able to show that the assumption concerned is quite justified. Since the publication of the paper by Ghosh, considerable amount of experimental analysis of tone quality has appeared in different registers. The present paper gives an account of the theoretical work in the light of our experimental investigation and also in the light of experimental analysis of tone quality by others. Considerable light is thrown on the performance of the reed with regard to tone quality and the presence of even harmonics.

To get visual access to the reed while it is vibrating and causing production of tone an artificial embouchure with transparent windows working on a similar principle as that of McGinnis and Gallagher was designed. The above authors have described the arrangement in detail, hence we need not give it here. In order to study the mode of vibration of the reed, parallel beam of sunlight was made to pass through an extremely narrow slit and the plane of the emerging light was arranged such that it cut transversely a section of the reed and that of the tip of the mouthpiece. Light was obstructed by the section of the reed and the tip and passed through the chink between them. The embouchure was tilted slightly in such a way that the rays of light became parallel to the flat table of the mouthpiece in which case the length of the light beam through the chink was maximum. In order to eliminate chromatic aberration the lens of a good camera was used. The reed was now set in vibration and the photograph taken moving the plate quickly with uniform speed. The section, of which the photograph was taken, was chosen to be very near the tip. A portion of the photograph was enlarged several times and Fig. 1 was drawn out of it. It can be seen that the aperture between the mouthpiece and the reed is never closed. This point is of fundamental significance in so far as it goes to contradict

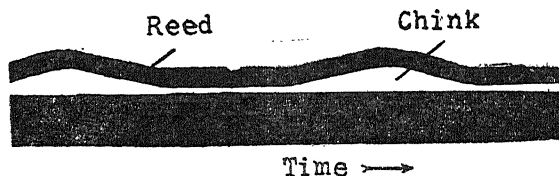


FIG. 1

McGinnis and Gallagher's stroboscopic observation and in so far as it goes to lend support to our present theory. Further the photograph shows that for practically one-half period the reed closes the aperture partially, with the chink-width remaining constant. In the other half period the reed vibrates practically sinusoidally.

In order to study the phase relationship between reed vibration and pressure vibration oscillogram of pressure variation just underneath the reed was taken. By making a delicate short-circuiting arrangement at the instances when the reed was maximum out, dots were obtained on the oscillogram. The circuit employed consisted of a carbon microphone in series with a battery and primary of a transformer the secondary of which was connected to an oscillograph. The shortcircuiting arrangement was incorporated in the secondary circuit. The current in the primary circuit being in phase with the pressure variation, the voltage in the secondary was  $90^\circ$  out of the phase with pressure variation. But for this  $90^\circ$  phase change, which ought to be taken into consideration, the dots correspond to the instances when the reed is maximum out. Fig. 2 shows the oscillogram of pressure variation just underneath the reed while *B Flat d* tone of the clarinet was being sounded ( $f = 267$  c.p.s.). The figure shows that the reed performs forced vibration with the same frequency as that of the fundamental of the tone emitted. This fact is in agreement with McGinnis and Gallagher's findings. Fig. 3 has been drawn with the help of Figs. 1 and 2 with proper  $90^\circ$  phase shifting and shows the phase relationship between the pressure variation just underneath the reed and the chink width variation. We find from this figure that air pressure is maximum when the chink is maximum open. This observation tallies with M. Carriere's<sup>3</sup> conclusion arrived at by studying coupling between a reed and air column according to which the air enters the tube when the reed gap is maximum. The figure also shows that for about the half period the reed partially closes the aperture the pressure underneath it is negative. We shall later on come back again to this figure when we compare it with our theoretical curve.

We now proceed to give the theory of clarinet we have developed on the assumption of partial closure of the aperture under the reed. We assume

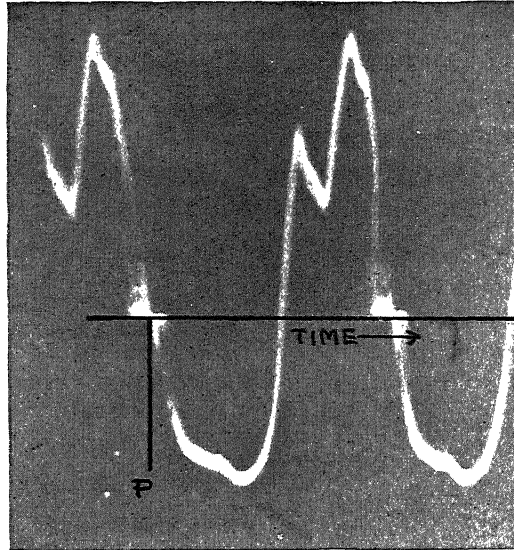


FIG. 2



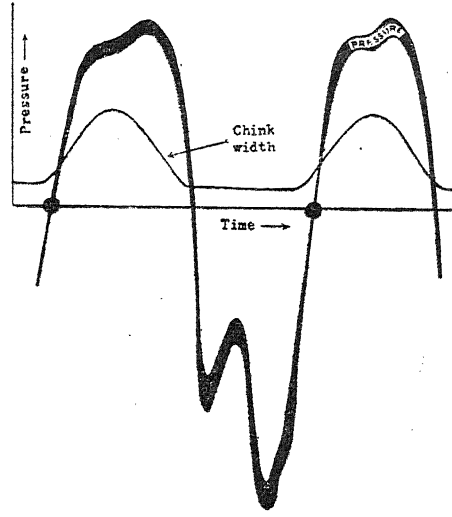


FIG. 3

a uniform bore of air chamber of radius  $a$  and length  $l$  and neglect radial vibrations in the pipe. We represent the solution of the wave equation for excess pressure  $p$  by Heaviside's method at any point  $x$  measured from the mouth.

$$p_x = \eta_1 \sinh \frac{\sigma}{c} x + \eta_2 \cosh \frac{\sigma}{c} x \quad (1)$$

where  $\sigma = \frac{d}{dt}$ ,  $c$  is the velocity of sound. The particle velocity  $u$  is given by

$$\sigma p u = - \frac{dp}{dx}$$

$$\text{i.e.,} \quad u = - \frac{1}{c\rho} \left\{ \eta_1 \cosh \frac{\sigma}{c} x + \eta_2 \sinh \frac{\sigma}{c} x \right\} \quad (2)$$

Hence at  $x = 0$ ,  $p = \eta_2$  and  $u = - \eta_1/c\rho$

And

$$p_l/u_l = - c\rho \left\{ \frac{\eta_1 \sinh \frac{\sigma}{c} l + \eta_2 \cosh \frac{\sigma}{c} l}{\eta_1 \cosh \frac{\sigma}{c} l + \eta_2 \sinh \frac{\sigma}{c} l} \right\} \quad (3)$$

where  $p_l$ ,  $u_l$  represent the pressure and particle velocity at  $x = l$  — the open end.

The solution of this on the assumption that the product  $Ky_0$  is small is

$$p = PQ \left[ S_0 + (\beta^2 m^2 + jam) y' + y (\beta^2 m^2 + jam) + \frac{cy'}{l} \sum \frac{e^{jm\omega_1 t}}{jm\omega_1} \right], \quad (4)$$

where  $\omega_1 = c/2l'$ ,  $K$  = conductivity of chink,  $y_0$  a permanent displacement of the reed,  $m$  an odd integer,  $\beta = \pi a/\sqrt{8}l$ ,  $\alpha = 4a/3l$ ,  $P$  the blowing pressure,  $Q = Kc\rho$ ,  $y' = (y_0 - AP/Mn^2)$ ,  $A$  being the effective surface of the reed.

In order to determine  $y$  we observe that the equation of motion of the reed is

$$(\sigma^2 + \frac{r}{M}\sigma + n^2)y = -\frac{(P-p)A}{M},$$

where  $r$  is the frictional force per unit velocity,  $M$  its effective mass, and  $n/2\pi$  its natural frequency.

Hence

$$y = -\frac{AP}{M\{n^2 - m^2\omega_1^2 + j\frac{r}{M}\}} + \frac{Q_1 cy'}{l} \sum \frac{e^{j\omega_1 mt}}{jm\omega_1 (n^2 - m^2\omega_1^2 + j\frac{r}{M})} \quad (5)$$

where  $Q_1 = APQ/M$ . Substituting this value of  $y$  in (4) we get

$$\begin{aligned} p = PQ & \left[ S_1 + Q_1 \beta^2 \frac{cy'}{l} \sum \frac{m^2 e^{jm\omega_1 t}}{jm\omega_1 (n^2 - m^2\omega_1^2 + j\frac{r}{M})} \right. \\ & + \frac{Q_1 \alpha cy'}{l} \sum \frac{m e^{jm\omega_1 t}}{m\omega_1 (n^2 - m^2\omega_1^2 + j\frac{r}{M})} \\ & \left. + \frac{cy'}{l} \sum \frac{e^{jm\omega_1 t}}{jm\omega_1} - \text{weak even harmonics} - \right], \quad (6) \end{aligned}$$

where it is assumed that  $S_1$  represents the sum of all the possible terms that are not periodic. The terms containing  $\beta^2$  may be neglected and thus we shall have,

$$\begin{aligned} p = PQ & \left[ S_1 + Q_1 \frac{\alpha cy'}{l\omega_1} \sum \frac{\cos \omega_1 mt}{(n^2 - m^2\omega_1^2 + j\frac{r}{M})} \right. \\ & \left. + \frac{cy'}{l} \sum \frac{\sinh m\omega_1 t}{m\omega_1} - \text{weak even harmonics} - \right]. \quad (7) \end{aligned}$$

It will be noticed that the coupling of the chink through which air is blowing at a constant pressure with the air column is sufficient to maintain the vibration of the air column. In the case of a vibrating reed having a very high natural frequency of vibration it does help in the manner expressed by the terms  $\sum \frac{\cos m_1 \omega_1 t}{(n^2 - m^2 \omega_1^2 + j \frac{r}{M})}$ . This means

that at the initial stage the compressional wave starts with the chink widened, and when it reaches back after reflection from the open end as rarefaction, the reed has performed half a vibration and has negative displacement, *i.e.*, towards the flat table closing the chink partially. This helps the reflection of the rarefaction from the partially closed end; at this instant the coupling of the mouthpiece with the vibrating air column has suddenly altered the pressure to a negative value. When the rarefaction reaches back as compression after reflection from the open end, the reed has performed another half vibration, and at this instant the reed has positive displacement, *i.e.*, the chink is widened. The widening of the chink allows more air to enter the mouthpiece and the compressional pressure is increased. It will be noticed that the reed performs forced vibration at a frequency  $n \sim m\omega_1$ , and in order to maintain the vibration this condition has to be realised. The reed has only one natural frequency on account of its chiseled shape. In practice the musicians adjust the frequency with care so that the frequency of the reed is in agreement with some odd component of the clarinet.

The flow of air is obtained easily from the results that

$$u = \frac{R}{c\rho} p \sim \frac{\beta^2 m^2}{c\rho} p$$

$$u = PQ \left[ S_2 + \frac{\beta^2 c y'}{l} \sum \frac{m^2 \cos m \omega_1 t}{(n^2 - m^2 \omega_1^2 + j \frac{r}{M})} \right. \\ \left. + \frac{c y'}{l} \sum \frac{m^2 \sin m \omega_1 t}{m \omega_1} \right].$$

If we sum only upto  $m = 11$ , the summation will not give infinitely large value. It will be noticed that the second term will vanish in the absence of vibration of reed, and then the coupling term  $\sum \frac{m^2 \sin m \omega_1 t}{m \omega_1}$  will remain, and will be sufficient to maintain the vibration of the air column. The presence of  $m^2$  in the numerator lends to the belief that the flow velocity

series will become divergent, *i.e.*, will give a very large value by taking  $m$  large. Since we sum upto  $m = 11$ , *i.e.*, 6 terms, the presence of the factor  $\beta^2$  does not allow the summation to obtain infinitely large value for the sum. These results hold good as long as  $ka < 1$ . The effect of vibration of the reed is mainly upon the quality of the note. It will be noticed that in the absence of vibration of the reed, the pressure changes will practically be given by the sum  $\sum \sin m\omega_1 t / m\omega_1$ . This summation will give nearly a constant positive pressure with fluctuations when six or seven terms are considered in the summation, *viz.*, from  $m = 1$  to  $m = 11$ , over a half cycle, and then suddenly changes to a negative value with similar fluctuations. At the end of the complete cycle the pressure again rises suddenly to a positive value. These changes are practically discontinuous. But the vibration of the reed through the terms  $\sum \frac{\cos m\omega_1 t}{\{n^2 - m^2\omega_1^2 + j \frac{r}{M}\}}$  introduces

larger fluctuations of pressure within the half cycle. The nearer  $n$  is to  $m\omega_1$ , the greater will be the modulations of pressure and hence more of the harmonics will be excited. In general  $n$  is large, say,  $n \sim 9\omega_1$ ; under these circumstances all those odd components near  $9\omega_1$  will be excited. It is possible to fix the value of  $n$  by adjusting the vibrating length of the reed, or by slight alteration of the same by the pressure of the lips upon the reed. Thus it will be noticed that the player can control the tone quality at pleasure.

The presence of weak even harmonics or a strong component corresponding to the natural frequency of the reed is easily brought out by the product terms which contain an abundance of weak even harmonics. Another point to be noticed is the dependence of the amplitude of the component on  $y''$ , *i.e.*,  $(y_0 - AP/Mn^2)$  which must be positive to ensure the adjustment of phase favourable for maintenance of vibration of the air column.

Fig. 4 has been drawn with the help of equation 7. On the assumption that the conditions prevailing at the time when Photograph No. 2 was taken were such as to make the fundamental in the summation of cosine series to be the dominating term. This would be the case when the natural frequency of the reed is adjusted to be of the same order as that of the fundamental of the tone. Further the amplitude of the term has been taken as 2.5 times that of the fundamental of the sine series and also it has been assumed that the damping introduces a phase change of  $\frac{1}{8}$ th period. We are justified to make these assumptions as the conditions are directly controllable by the player. Comparison of the pressure-time curve with

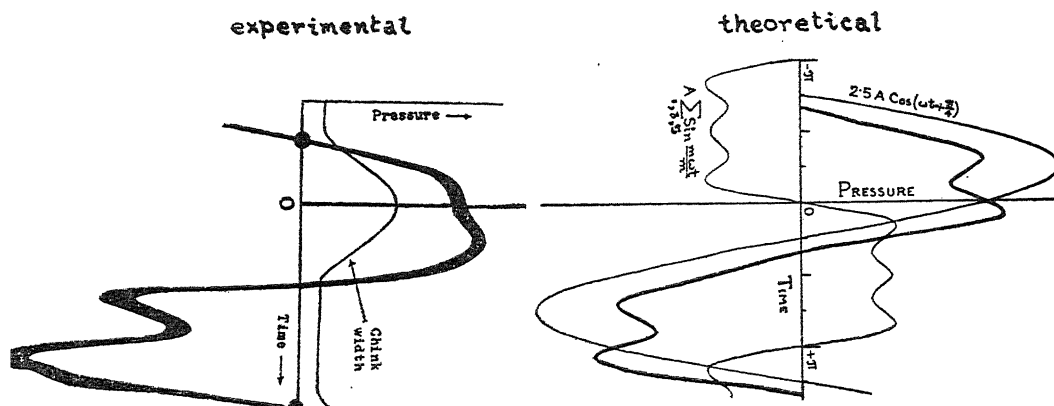


FIG. 4

that of our experimental curve (Fig. 3) shows great similarity as regards shape of the curve, discontinuous changes and also as regards phase-relationship between pressure variation and chink-width opening, the maximum opening of chink-width being corresponding to  $\omega t = 0$  in the above figure. Thus our experimental findings fully justify our theory.

I have to thank Dr. R. N. Ghosh for his valuable guidance during the progress of the work.

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# RADIAL OSCILLATIONS OF A POLYTROPIC MODEL OF INDEX 4

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## SUMMARY

The periods of the fundamental mode and first overtone have been found out for a polytropic model of index 4.

In a previous paper the author<sup>1</sup> studied the radial adiabatic oscillations of a gaseous star of polytropic index unity. The periods and the amplitudes of the displacements of the first three modes of pulsations were found out for that model. In the present note the radial oscillations of another polytropic model of index 4 has been studied. The periods of the fundamental mode and first overtone as well as the amplitudes of the displacements for the two modes have been found out for  $\alpha = 0.6$ , which corresponds to the ratio of specific heats  $\gamma = 5/3$ . Miller (1929) has also found out the period of the fundamental mode for this model taking  $\alpha = 0.2$ , which corresponds to  $\gamma = 10/7$ . The choice of such a low value for  $\alpha$  was due to the 'belief current at that time that radiant heat makes up a large part of the total thermal energy, and that the low ratio of specific heats of radiation ( $\gamma = 4/3$ ) contributes materially to the mean value of  $\gamma$ '. However, no physical justification for such a low value of  $\gamma$  (1.43) is at present apparent.

The differential equation for small radial adiabatic oscillation as given by Eddington,<sup>2</sup> is

$$\frac{d^2 f}{dz^2} + \frac{4 - \mu}{z} \frac{df}{dz} + \left( \frac{\omega^2}{u} - \frac{\alpha \mu}{z^2} \right) f = 0, \quad (1)$$

where  $f$  is the amplitude of the displacement  $\frac{d\xi}{\xi}$ ,  $z$  is proportional to  $\xi$ , mean distance from the centre,  $\alpha = 3 - 4/\gamma$ .  $\gamma$  being the ratio of specific heats,  $\mu = \frac{g_0 \rho_0 z}{P_0}$ ,  $\omega^2 = \nu^2 \left( \frac{5}{4\pi G \rho_c \gamma} \right)$ , the period  $\Pi = \frac{2\pi}{\nu}$ , and  $u$  is the Emden function of the polytrope  $n = 4$ ;  $g_0$ ,  $\rho_0$ ,  $P_0$  being respectively the equilibrium values of gravity, density and pressure at a distance  $z$  from the centre,  $G$  the constant of Gravitation and  $\rho_c$  the mean density at the centre.

Emden equation for the polytrope  $n = 4$ , is

$$\frac{d^2u}{dz^2} + \frac{2}{z} \frac{du}{dz} + u^4 = 0. \quad (2)$$

This equation has been solved by the usual power series. The various coefficients are found out from the relations amongst the coefficients and  $u$  for the polytrope  $n = 4$ , is found to be

$$u = 1 - \frac{1}{6} z^2 + \frac{1}{30} z^4 - \frac{1}{140} z^6 + \frac{43}{27216} z^8 \dots \quad (3)$$

From Emden's theory  $\mu = -(n+1) \frac{z}{u} \frac{du}{dz}$ .

Using the value of  $\mu$ , the equation (1) will be

$$\frac{d^2f}{dz^2} + \left( \frac{4}{z} + \frac{5}{u} \frac{du}{dz} \right) \frac{df}{dz} + \left( \frac{\omega^2}{u} + \frac{5a}{zu} \frac{du}{dz} \right) f = 0 \quad (4)$$

This equation has singularities both at the centre and the surface, and a non-singular solution is possible for certain values of  $\omega^2$ , which is to be found out by a method of trial.

The values for starting the integrations are found out from the series solutions near the centre. For the neighbourhood of  $z = 0$  and  $z$  at the surface of the star equation (4) was solved by the power series. The expansion for  $u$  near the centre given by equation (3), with its help the solution in series for  $f$  is easily found to be

$$f = a_0 + a_2 z^2 + a_4 z^4 + a_6 z^6 + a_8 z^8 + \dots \quad (5)$$

where the various coefficients  $a_0, a_2, a_4, a_6, \dots$  are given by the relation

$$\begin{aligned} a_2 &= \frac{1}{10} \left\{ \frac{5a}{3} - \omega^2 \right\} a_0 \\ a_4 &= \frac{1}{28} \left\{ \left( 5 + \frac{5a}{3} - \omega^2 \right) a_2 - \frac{2a}{3} a_0 \right\} \\ a_6 &= \frac{1}{54} \left\{ \left( \frac{34}{3} + \frac{5a}{3} - \omega^2 \right) a_4 - \left( \frac{5}{3} + \frac{2a}{3} \right) a_2 + \frac{3a}{14} a_0 \right\} \\ a_8 &= \frac{1}{88} \left\{ \left( 19 + \frac{5a}{3} - \omega^2 \right) a_6 - \left( \frac{18}{5} + \frac{2a}{3} \right) a_4 \right. \\ &\quad \left. + \left( \frac{1}{2} + \frac{3a}{14} \right) a_2 - \frac{215a}{3402} a_0 \right\} \end{aligned}$$

Near the boundary of the star  $u$  may be expanded by Taylor's theorem in powers of  $\xi$ , where  $\xi = \frac{\xi_R - z}{\xi_R}$ ,  $\xi_R$  is the radius of the star, we get

$$u = p \{ \xi + \xi^2 + \xi^3 + (1 - \frac{1}{6}q) \xi^4 + \dots \} \quad (6)$$

where

$$p = -\xi_R \left( \frac{du}{dz} \right)_R, \quad q = -\xi_R^3 \left( \frac{d^2u}{dz^2} \right)_R \quad (7)$$

Substituting equations (6) and (7) in equation (4) and taking

$$f = b_0 + b_1\xi + b_2\xi^2 + b_3\xi^3 + b_4\xi^4 + \dots$$

we get, by putting the various coefficients equal to zero,

$$b_1 = -\frac{1}{5}(\omega_0 - 5a)$$

$$b_2 = \frac{1}{12} \{ (5a - 1 - \omega_0) b_1 + (\omega_0 + 10a) b_0 \}$$

$$b_3 = \frac{1}{21} \{ (5a - 2 - \omega_0) b_2 + (\omega_0 + 10a - 1) b_1 + 15ab_0 \}$$

$$b_4 = \frac{1}{32} [ (5a - 3 - \omega_0) b_3 + (\omega_0 + 10a - 2) b_2 + (15a - 1 + 10/3 q) b_1 + 20a (1 - \frac{1}{6} q) b_0 ],$$

$$\text{where } \omega_0 = -\frac{\omega^2 \xi_R}{\left( \frac{du}{dz} \right)_R}$$

The integrations were carried out for  $\alpha = 0.6$ , and the interval  $h$  was chosen to be 0.2. For the series expansions coefficients were calculated up to  $a_8$ , and these values were used to compute  $f$  at  $z = 0, 0.2, 0.4, 0.6$  respectively; with these starting values the integrations of the equation (4) have been performed numerically. The method of integration has already been referred to in the previous paper by the author. The integrations were started with the arbitrary amplitude  $f = 1$  at the centre and the solution is continued towards the surface till it is evident how the solution behaves at the surface. The method is quite sensitive as a change in the fifth decimal place for a value of  $\omega^2$  would show, if it is a correct solution, a steady increase in the displacement functions from the centre right up to the surface of the star, whereas adjacent solutions show either abrupt increase or decrease near the surface. The characteristic value of  $\omega^2$  for the fundamental mode is found out in



this way. For the first overtone, it has been found that the displacement function increases up to near about two-third of the radius of the star, and then decreases.

Table I gives the characteristic values of  $\omega^2$ . Table II gives the amplitudes of the displacements as functions of the mean distance from the centre, normalised so that the amplitude at the surface of the star is unity.

TABLE I  
*Characteristic Values of  $\omega^2$*

Mode	$\alpha = 0.6$
0	0.02434
1	0.04006

TABLE II  
*Amplitudes of the Displacements,  $f$*

$z$	Fundamental ( $\alpha = 0.6$ )	First overtone ( $\alpha = 0.6$ )	$z$	Fundamental ( $\alpha = 0.6$ )	First overtone ( $\alpha = 0.6$ )
0.0	+0.000166	-0.000114	4.2	+0.000920	-0.000588
0.2	+0.000167	-0.000115	4.4	+0.001060	-0.000672
0.4	+0.000169	-0.000116	4.6	+0.001224	-0.000767
0.6	+0.000172	-0.000118	4.8	+0.001413	-0.000877
0.8	+0.000177	-0.000121	5.0	+0.001634	-0.001002
1.0	+0.000183	-0.000126	5.2	+0.001889	-0.001144
1.2	+0.000192	-0.000131	5.4	+0.002184	-0.001305
1.4	+0.000202	-0.000138	5.6	+0.002524	-0.001487
1.6	+0.000215	-0.000147	5.8	+0.002917	-0.001692
1.8	+0.000231	-0.000157	6.0	+0.003369	-0.001922
2.0	+0.000250	-0.000170	6.2	+0.003889	-0.002179
2.2	+0.000272	-0.000185	6.4	+0.004485	-0.002465
2.4	+0.000300	-0.000203	6.6	+0.005169	-0.002783
2.6	+0.000332	-0.000224	6.8	+0.005952	-0.003133
2.8	+0.000371	-0.000249	7.0	+0.006848	-0.003518
3.0	+0.000416	-0.000278	7.2	+0.007872	-0.003939
3.2	+0.000470	-0.000312	7.4	+0.009039	-0.004396
3.4	+0.000534	-0.000352	7.6	+0.010371	-0.004890
3.6	+0.000609	-0.000399	7.8	+0.011887	-0.005418
3.8	+0.000697	-0.000453	8.0	+0.013616	-0.005980
4.0	+0.000800	-0.000516	8.2	+0.015573	-0.006569

TABLE II—(Continued)

$z$	Fundamental ( $\alpha = 0.6$ )	First overtone ( $\alpha = 0.6$ )	$z$	Fundamental ( $\alpha = 0.6$ )	First overtone ( $\alpha = 0.6$ )
8.4	+0.017805	-0.007182	11.8	+0.152914	+0.015310
8.6	+0.020329	-0.007807	12.0	+0.172897	+0.024941
8.8	+0.023200	-0.008436	12.2	+0.194189	+0.036978
9.0	+0.026443	-0.009048	12.4	+0.218690	+0.052204
9.2	+0.030127	-0.009628	12.6	+0.246024	+0.071144
9.4	+0.034273	-0.010139	12.8	+0.278852	+0.095341
9.6	+0.038977	-0.010557	13.0	+0.310876	+0.123412
9.8	+0.044284	-0.010833	13.2	+0.351306	+0.159664
10.0	+0.050291	-0.010916	13.4	+0.387764	+0.199505
10.2	+0.057079	-0.010738	13.6	+0.448257	+0.258693
10.4	+0.064653	-0.010200	13.8	+0.498747	+0.320386
10.6	+0.073343	-0.009234	14.0	+0.575834	+0.420834
10.8	+0.082980	-0.007675	14.2	+0.637134	+0.497491
11.0	+0.093918	-0.005397	14.4	+0.693338	+0.591343
11.2	+0.106031	-0.002201	14.6	+0.817530	+0.751987
11.4	+0.120114	+0.002125	14.8	+0.915619	+0.886532
11.6	+0.135731	+0.007867	14.9715	+1.000000	+1.000000

The characteristic values of  $\omega^2$  were determined in the following way. A trial value of  $\omega^2$  was chosen, then the integrations were performed taking  $\gamma = 5/3$ . It was possible to narrow down the trial values of  $\omega^2$  from a few steps of the integrations, where it was found that the displacement functions are either tending to positive or negative infinity. For the higher mode the trial values were estimated from the fact that their periods do not vary much from model to model. The final integrations from the centre to the surface of the star were made for the following values of  $\omega^2$ :

0.0246, 0.0240, 0.0243, 0.02438, 0.02434; 0.040, 0.041, 0.04012, 0.04006.

The final values of  $\omega^2$  and the amplitudes of the first two modes are given in the tables. All the calculations were done with the help of *Mathematical Tables II (1946) of the British Association for the Advancement of Science* and the calculating machine.

I am grateful to Prof. A. C. Banerji for his keen interest in this paper.

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# OXIDATION OF COAL IN SOIL WITH OR WITHOUT EASILY OXIDISABLE ORGANIC MATERIAL

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IN our previous communication<sup>1</sup> we had discussed the oxidation of carbon of the coal when added to soil in very finely divided condition. It was observed that the coals undergo slow oxidation at the ordinary temperature more so in light than in the dark. In this paper the results obtained on the addition of coals to soil with and without straw or sugar are recorded in the tables in the following manner:—

Experimental procedure is the same as described in our previous paper.<sup>1</sup> The straw or sugar was powdered well and passed through 0.5 mm. sieve before mixing to soil.

Analysis of materials used:—

	Total carbon %	Total nitrogen %
Soil .. .. .	0.514	0.0645
Straw .. .. .	41.4	0.6210
Sugar .. .. .	39.8	0.4960
	On ash-free basis	On ash-free basis
Lignite (Palana) ..	68.4	0.77
Bituminous coal (Jharia)	88.8	1.53
Anthracite coal (Jammu)	83.4	1.29

TABLE I

TABLE II

Period of exposure in days	State	Soil control 250 gm.		Soil + Lignite (Palana) 250 gm. 5 gm.	
		Total carbon % on dry basis in gm.	% of carbon oxidised	Total carbon % on dry basis in gm.	% of carbon oxidised
0	Exposed	0.514	..	1.8349	..
	Covered	0.514	..	1.8349	..
90	Exposed	0.480	6.6	1.704	7.6
	Covered	0.500	2.7	1.756	4.3
180	Exposed	0.452	12.0	1.575	14.1
	Covered	0.493	6.0	1.680	8.6
270	Exposed	0.445	13.4	1.439	21.1
	Covered	0.471	8.3	1.594	13.5
360	Exposed	0.438	14.7	1.303	29.0
	Covered	0.460	10.5	1.505	18.0

TABLE III

TABLE IV

Period of exposure in days	State	Soil + Bituminous coal (Jharia) 250 gm. 5 gm.		Soil + Anthracite (Jammu) 250 gm. 5 gm.	
		Total carbon % on dry basis in gm.	% of carbon oxidised	Total carbon % on dry basis in gm.	% of carbon oxidised
0	Exposed	2.096	..	1.602	..
	Covered	2.096	..	1.602	..
90	Exposed	2.042	2.8	1.574	1.8
	Covered	2.063	1.9	1.590	0.6
180	Exposed	1.986	5.2	1.549	3.1
	Covered	2.048	2.3	1.579	1.3
270	Exposed	1.941	6.9	1.513	5.6
	Covered	2.008	4.9	1.562	2.5
360	Exposed	1.887	10.0	1.480	7.5
	Covered	1.973	6.0	1.548	3.8

TABLE V

Period of exposure in days	State	Soil + Sugar 250 gm. 5 gm.		Soil + Sugar + Lignite 250 gm. 5 gm. 5 gm.	
		Total carbon % on dry basis in gm.	% of carbon oxidised	Total carbon % on dry basis in gm.	% of carbon oxidised
0	Exposed	1.259	..	2.478	..
	Covered	1.259	..	2.478	..
90	Exposed	0.755	39.6	1.895	23.3
	Covered	0.705	43.6	2.064	17.2
180	Exposed	0.648	48.4	1.428	42.3
	Covered	0.627	50.0	1.767	28.6
270	Exposed	0.583	53.9	1.073	56.8
	Covered	0.575	54.0	1.502	39.5
360	Exposed	0.534	59.0	0.793	68.0
	Covered	0.528	60.0	1.264	49.0

TABLE VI

TABLE VII

TABLE VIII

Period of exposure in days	State	Soil + Sugar + Bituminous coal (Jharia) 250 gm. 5 gm. 5 gm.			Soil + Sugar + Anthracite (Jammu) 250 gm. 5 gm. 5 gm.		
		Total carbon % on dry basis in gm.	% of carbon oxidised		Total carbon % on dry basis in gm.	% of carbon oxidised	
0	Exposed	2.784	..		2.326	..	
	Covered	2.784	..		2.326	..	
90	Exposed	2.187	21.2		1.829	21.4	
	Covered	2.395	13.6		1.965	15.4	
180	Exposed	1.692	39.2		1.453	37.7	
	Covered	2.058	25.9		1.724	26.1	
270	Exposed	1.359	51.0		1.145	50.6	
	Covered	1.825	34.1		1.541	33.9	
360	Exposed	1.058	62.0		0.942	59.5	
	Covered	1.670	40.0		1.419	39.0	

TABLE IX

Period of exposure in days	State	Soil + Straw 250 gm. 5 gm.		Soil + Straw + Lignite 250 gm. 5 gm. 5 gm.	
		Total carbon % on dry basis in gm.	% of carbon oxidised	Total carbon % on dry basis in gm.	% of carbon oxidised
0	Exposed	1.136	..	2.416	..
	Covered	1.136	..	2.416	..
90	Exposed	0.908	20.1	1.975	19.3
	Covered	0.896	21.0	2.086	13.6
180	Exposed	0.791	30.7	1.662	31.4
	Covered	0.775	32.4	1.884	22.3
270	Exposed	0.702	38.5	1.396	42.1
	Covered	0.689	49.4	1.717	28.9
360	Exposed	0.624	45.6	1.1597	52.0
	Covered	0.608	46.5	1.5580	35.5

TABLE XI

Period of exposure in days	State	Soil + Straw + Bituminous 250 gm. 5 gm. coal (Jharia) 5 gm.			Soil + Straw + Anthracite 250 gm. 5 gm. (Jammu) 5 gm.		
		Total carbon % on dry basis in gm.	% of carbon oxidised		Total carbon % on dry basis in gm.	% of carbon oxidised	
0	Exposed	2.738	..		2.211	..	
	Covered	2.738	..		2.211	..	
90	Exposed	2.363	14.9		1.876	14.9	
	Covered	2.425	11.3		1.938	12.2	
180	Exposed	2.033	25.9		1.607	27.1	
	Covered	2.176	20.4		1.731	21.7	
270	Exposed	1.741	36.4		1.395	36.6	
	Covered	1.989	28.9		1.588	28.0	
360	Exposed	1.479	46.0		1.238	44.0	
	Covered	1.835	33.0		1.459	34.0	

The results show that lignite, bituminous coal and anthracite coal are oxidised when mixed with soil and the oxidation of carbon is in the following order—lignite (maximum), bituminous coal (next) and anthracite coal (least).

When a mixture of sugar or straw and coal is added to soil and allowed to oxidise, the straw and sugar are oxidised at a faster rate than the coal. In the following tables the per cent. oxidation of coal alone, straw alone, and sugar alone along with their mixture has been recorded.

Variety of coal		Period of exposure in days	Coal carbon oxidised	Sugar carbon oxidised	Carbon oxidised of the mixture of coal and sugar	
					Observed	Calculated
Lignite (Palana)	..	180	0.260	0.611	1.050	0.871
		270	0.396	0.676	1.405	1.072
		360	0.532	0.725	1.684	1.257
Vide Tables ..	..		II	V	VI	
Bituminous coal (Jharia)		180	0.110	0.611	1.092	0.721
		270	0.155	0.676	1.425	0.831
		360	0.209	0.725	1.726	0.934
Vide Tables ..	..		III	V	VII	
Anthracite coal (Jammu)		180	0.053	0.611	0.873	0.664
		270	0.089	0.676	1.181	0.765
		360	0.122	0.725	1.384	0.847
Vide Tables ..	..		IV	V	VIII	

Variety of coal mixed		Period of exposure in days	Coal carbon oxidised	Straw carbon oxidised	Carbon oxidised of the mixture of coal and straw	
					Observed	Calculated
Lignite (Palana)	..	180	0.260	0.345	0.754	0.605
		270	0.396	0.434	1.020	0.830
		360	0.532	0.512	1.256	1.044
Vide Tables ..	..		II	IX	X	
Bituminous coal (Jharia)		180	0.110	0.345	0.705	0.455
		270	0.155	0.434	0.997	0.589
		360	0.209	0.512	1.260	0.721
Vide Tables ..	..		III	IX	XI	
Anthracite coal (Jammu)		180	0.053	0.345	0.604	0.398
		270	0.089	0.434	0.816	0.523
		360	0.122	0.512	0.973	0.634
Vide Tables ..	..		IV	IX	XII	

Note.—All the figures are of light exposed set. The quantity of carbon oxidised in 100 gm. of mixture is shown.

The foregoing results clearly show that the carbon in the mixture of coal and sugar or the mixture of coal and straw with soil is oxidised with greater ease than the two ingredients considered separately. These experimental observations are of the same type as those observed by F. E. Broadbent<sup>2</sup> using Sudan grass as manure. He observed that the decomposition of Sudan grass when mixed with soil appreciably intensifies the decomposition of soil humus.

In researches carried on in these laboratories, it has been observed that the velocity of oxidation of energy materials is greater in sand than in soil under identical conditions. Sand being more porous presents more surface which facilitates oxidation. It seems that the introduction of coal to soil makes the soil more porous and thus the oxidation is facilitated. The straw also increases the porosity of soil and helps the oxidation.

#### SUMMARY

The carbon in the mixture of coal and straw or the mixture of coal and sugar with soil is oxidised with greater ease than the two ingredients considered separately.

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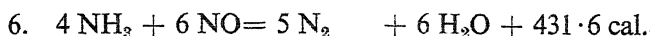
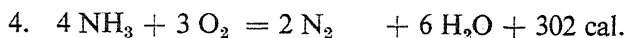


# NITROGEN LOSS FROM THE OXIDATION OF NITROGENOUS COMPOUNDS BY HYDROGEN-PEROXIDE IN PRESENCE AND ABSENCE OF METALLIC COPPER

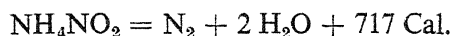
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It is well known that the following reactions take place between ammonia and oxygen in the oxidation of ammonia:—



According to Neumann and Rose 90% of oxidation products consist of nitrous acid when ammonia burns in air. In presence of oxygen 70–80% of nitric acid and 20–30% nitrous acid is formed in the oxidation of ammonia. It is clear therefore that along with the above chemical changes there is always the possibility of the occurrence of the following reaction which leads to the formation of gaseous nitrogen even at the ordinary temperature:



Hence in the oxidation of ammonia there is the formation of the nitrogen gas with reduction in the production of nitric acid.

For a number of years we have been carrying on extensive research work on the slow oxidation of ammonium salts and other nitrogenous compounds by air in presence of soil or chemical compounds like iron oxide, zinc oxide, etc. We have observed that with ammonium salts and other nitrogenous compounds there is considerable loss of nitrogen more in the light than in the dark as shown below:

Substance mixed with soil	Period of exposure in months	% loss of nitrogen		% loss of nitrogen in unit time (per month)	
		Light	Dark	Light	Dark
Ammonium sulphate ..	2	55.5	43.2	27.8	21.5
Ammonium phosphate	2	67.5	58.4	33.8	29.2
Ammonium nitrate ..	2	28.9	21.0	14.5	10.5
Ammonium tartrate ..	2	47.6	38.3	23.8	19.2
Ammonium oxalate ..	2	36.6	28.6	18.3	14.3
Ammonium citrate ..	4½	69.3	54.8	22.1	12.2
Urea ..	3½	47.4	35.1	10.5	7.8
Hippuric acid ..	4½	42.3	23.2	9.4	5.2
Gelatine ..	4½	40.1	23.2	8.9	5.2
Oil-cake ..	5½	35.9	29.0	6.5	5.3
Blood ..	6	54.1	48.7	9.0	8.1

We have explained the loss in the nitrification of nitrogenous compounds in soil at the ordinary temperature due to the formation and decomposition of the unstable substance ammonium nitrite.

In soils when ammonium salts, uric acid, urea, blood, oilcakes, are added the first products are amino acids from proteins and these undergo oxidation to ammonia which oxidises slowly to nitrite and nitrate. It is clear therefore that in soil or in presence of chemical surface at the ordinary temperature the whole of the ammonia or the ammonium salt produced or added cannot be readily converted into nitrate. Hence  $\text{NH}_4$  ions and occasionally free ammonia have to co-exist with nitrite ion or nitrous acid and thus decomposition takes place with evolution of nitrogen. The evolution of nitrogen from nitrogenous compounds in soil or in surfaces has to be more pronounced than in the catalytic industrial oxidation of ammonia, because the oxidation of ammonia at high temperature in presence of platinum to nitric acid has a high velocity than at the ordinary temperature in soils or in presence of chemical surfaces. In the Ostwald method of manufacture of ammonia with platinum as catalyst the gaseous mixture of ammonia and air is passed as rapidly as possible over the catalyst and hence the ammonia

is oxidised as quickly as possible to nitric acid so that there is no chance of the co-existence of ammonia, nitrous acid,  $\text{NO}_2$ , etc., and thus the possibility of the formation and decomposition of the unstable substance ammonium nitrite is greatly reduced. The real point for increasing the yield of nitric acid is to convert the ammonia into its oxidised product nitric acid as quickly as possible. In non-platinum catalysts, the velocity of the oxidation of ammonia to nitric acid is not very high and hence the yield of nitric acid is less than in platinum process.

As the abovementioned chemical change is of considerable theoretical and practical importance we have undertaken the oxidation of ammonia, ammonium salts, urea, uric acid, amino acids, proteins and other nitrogenous compounds by air at the ordinary temperature or by oxidising agents like hydrogen peroxide, potassium permanganate, etc., in presence or absence of catalysts. In the following pages, some results on the oxidation of ammonium salts by hydrogen peroxide in presence and absence of copper as catalyst are given.

#### EXPERIMENTAL PROCEDURE

Ammonium salt solutions were prepared of about 1% nitrogen content. To known volumes of each of these solutions hydrogen peroxide (20 vol.) was added. The solutions were then heated on water-bath for a definite period and the ammoniacal and nitric nitrogen of the solution was estimated by the standard methods of analysis.

The total nitrogen was determined by reduction with Devardas alloy and distillation with alkali, the standard acid being titrated against standard alkali solution and nitrogen calculated by difference. The ammonia was determined by distillation with magnesia and nitric nitrogen together with nitrite nitrogen was calculated by difference. The results in the tables show combined nitrate and nitrite nitrogen. The maximum error of the estimation was 2%.

*Note.*—In the Tables I-XVI, under column "Treatment,"

$T_1$	means	100 c.c. O.S. + 25 c.c. $\text{H}_2\text{O}_2$ (20 vol.),	heated for 1 hour on water-bath.	
$T_2$	"	"	+ 25 c.c. "	" 2 hours "
$T_3$	"	"	+ 50 c.c. "	" 1 hour "
$T_4$	"	"	+ 50 c.c. "	" 2 hours "
$T_5$	"	"	+ 25 c.c. " + 0.5 gm. copper "	" 1 hour "
$T_6$	"	"	+ 25 c.c. " + "	" 2 hours "
$T_7$	"	"	+ 50 c.c. " + "	" 1 hour "
$T_8$	"	"	+ 50 c.c. " + "	" 2 hours "

TABLE I

*Ammonium Phosphate*(O.S. containing 1.004 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate
$T_1$	0.902	0.052	0.954	5.0	5.2
$T_2$	0.898	0.052	0.950	5.0	5.2
$T_3$	0.907	0.048	0.955	5.0	4.8
$T_4$	0.901	0.046	0.947	5.5	4.6

TABLE II

*Ammonium Oxalate*(O.S. containing 0.9838 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate
$T_1$	0.908	0.036	0.944	5.0	3.6
$T_2$	0.901	0.034	0.935	6.0	3.4
$T_3$	0.906	0.032	0.938	5.5	3.2
$T_4$	0.895	0.036	0.931	6.5	3.6

TABLE III

*Ammonium Acetate*(O.S. containing 0.9936 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate
$T_1$	0.912	0.034	0.946	5.0	3.0
$T_2$	0.909	0.034	0.943	5.0	3.4
$T_3$	0.899	0.028	0.927	8.0	2.8
$T_4$	0.871	0.030	0.901	9.0	3.0

TABLE IV

*Ammonium Citrate*

(O.S. containing 0.940 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate
$T_1$	0.765	0.076	0.841	11.0	7.6
$T_2$	0.769	0.044	0.813	14.0	4.4
$T_3$	0.709	0.040	0.749	20.0	4.0
$T_4$	0.756	0.044	0.800	15.0	4.4

TABLE V

*Ammonium Sulphate*

(O.S. containing 0.969 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate
$T_1$	0.875	0.038	0.913	6.5	3.8
$T_2$	0.873	0.032	0.905	7.0	3.2
$T_3$	0.888	0.026	0.914	6.5	2.6
$T_4$	0.876	0.036	0.912	6.5	3.6

TABLE VI

*Ammonium Chloride*

(O.S. containing 0.956 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate
$T_1$	0.886	0.020	0.906	6.5	2.0
$T_2$	0.881	0.030	0.911	6.0	3.0
$T_3$	0.871	0.032	0.903	6.5	3.2
$T_4$	0.877	0.020	0.897	7.0	2.0

TABLE VII  
*Ammonium Nitrate*

(O.S. containing 1.084 % Nitrogen as  $\text{NH}_3\text{-N}$  &  $\text{NO}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate	Weight of copper dissolved
$T_1$	0.461	0.554	1.015	7.0	2.1	..
$T_2$	0.459	0.557	1.016	7.0	2.2	..
$T_3$	0.454	0.563	1.017	7.0	2.5	..
$T_4$	0.459	0.545	1.004	7.5	2.0	..

TABLE VIII  
*Ammonium Dichromate*

(O.S. containing 1.161 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate	Weight of copper dissolved
$T_1$	1.078	0.040	1.118	4.0	4.0	..
$T_2$	1.059	0.048	1.107	5.0	4.8	..
$T_3$	1.035	0.046	1.081	7.5	4.6	..
$T_4$	1.052	0.040	1.092	6.5	4.0	..

TABLE IX  
*Ammonium Phosphate*

(O.S. containing 1.004 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate	Weight of copper dissolved
$T_5$	0.850	0.082	0.932	7.0	8.2	0.0225
$T_6$	0.848	0.076	0.924	7.5	7.6	0.0351
$T_7$	0.864	0.061	0.925	7.5	6.1	0.0281
$T_8$	0.843	0.077	0.920	8.0	7.7	0.0235

TABLE X  
*Ammonium Oxalate*

(O.S. containing 0.9839 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate	Weight of copper dissolved
$T_5$	0.777	0.056	0.833	16.0	5.6	0.1246
$T_6$	0.743	0.058	0.801	18.0	5.8	0.1198
$T_7$	0.779	0.048	0.827	17.0	4.8	0.0912
$T_8$	0.768	0.054	0.822	17.0	5.4	0.0948

TABLE XI  
*Ammonium Acetate*

(O.S. containing 0.9936 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate	Weight of copper dissolved
$T_5$	0.884	0.048	0.932	6.0	4.8	0.0212
$T_6$	0.888	0.042	0.930	6.0	4.2	0.0402
$T_7$	0.887	0.034	0.921	7.0	3.4	0.0200
$T_8$	0.885	0.038	0.923	7.0	3.8	0.0304

TABLE XII  
*Ammonium Citrate*

(O.S. containing 0.940 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate	Weight of copper dissolved
$T_5$	0.488	0.127	0.615	35.0	12.7	0.1330
$T_6$	0.499	0.082	0.582	37.0	8.2	0.1318
$T_7$	0.353	0.070	0.423	56.0	7.0	0.1874
$T_8$	0.257	0.100	0.357	65.0	10.0	0.1666

TABLE XIII

*Ammonium Sulphate*(O.S. containing 0.969 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{O}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate	Weight of copper dissolved
$T_5$	0.868	0.042	0.910	6.0	4.2	0.0156
$T_6$	0.860	0.042	0.902	7.0	4.2	0.0160
$T_7$	0.865	0.034	0.899	7.0	3.4	0.0162
$T_8$	0.861	0.040	0.901	7.0	4.0	0.0116

TABLE XIV

*Ammonium Chloride*(O.S. containing 0.956 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate	Weight of copper dissolved
$T_5$	0.854	0.054	0.908	6.5	5.4	0.0266
$T_6$	0.858	0.054	0.912	6.0	5.4	0.0260
$T_7$	0.865	0.036	0.901	6.5	3.6	0.0390
$T_8$	0.880	0.024	0.904	6.5	2.4	0.0274

TABLE XV

*Ammonium Nitrate*(O.S. containing 1.084 % Nitrogen as  $\text{NH}_3\text{-N}$  &  $\text{NO}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate	Weight of copper dissolved
$T_5$	0.462	0.458	0.920	15.0	..	0.0032
$T_6$	0.454	0.450	0.904	16.0	..	0.0040
$T_7$	0.450	0.446	0.896	17.0	..	0.0041
$T_8$	0.449	0.446	0.895	17.0	..	0.0043



TABLE XVI

*Ammonium Dichromate*(O.S. containing 1.161 % Nitrogen as  $\text{NH}_3\text{-N}$ )

Treat- ment	$\text{NH}_3\text{-N}$ % after treat- ment	$\text{NO}_3\text{-N}$ % after treat- ment	Total nitrogen % after treatment	% of nitrogen lost in treatment	% of nitrogen oxidised to nitrate	Weight of copper dissolved
$T_5$	1.026	0.076	1.102	5.0	7.5	0.0000
$T_6$	1.033	0.072	1.105	5.0	7.1	0.0000
$T_7$	1.038	0.070	1.108	5.0	7.0	0.0000
$T_8$	1.007	0.080	1.087	7.0	7.8	0.0000

When copper is added to ammonium salt solutions like ammonium oxalate or ammonium acetate, it goes into solution when heated in presence of hydrogen peroxide. Metallic copper was tried as a catalyst in the above oxidation reaction of ammonium salts by hydrogen peroxide. To known volumes of the ammonium salt solutions, hydrogen peroxide (20 vol.) and 0.5 gm. metallic copper were added and solutions heated on water-bath as previously. The ammoniacal and nitric nitrogen were estimated in these solutions, along with the quantity of copper went in solution. Copper was found to react slightly with ammonium chloride solution of all the ammonium salts used, when tried alone. The results are recorded in Tables IX-XVI.

It is evident from the foregoing results that the ammonium salts are oxidised by hydrogen peroxide. The oxidation is maximum in case of ammonium citrate, next come ammonium phosphate, ammonium dichromate and the rest of the ammonium salts used. The loss of nitrogen is nearly the same (between 5-7%) in all the cases (*vide* Tables I-VIII) except with ammonium citrate which is 15%.

When metallic copper is added to ammonium salt solutions along with hydrogen peroxide, it is observed that the oxidation of ammonium salts to nitrate is increased (compare Tables I-VIII and IX-XVI). The maximum oxidation in presence of copper is observed with ammonium citrate, about 12%. The loss of nitrogen also is maximum with ammonium citrate but increase of loss of nitrogen is also observed with ammonium oxalate and ammonium nitrate.

One peculiar point is observed that the increase of quantity of hydrogen peroxide or the heating period or both, does not affect the oxidation of

ammonium salts. Rather the loss of nitrogen is increased by prolonged heating which is more prominent in case of ammonium citrate. Also, the quantity of copper dissolved during the treatment seems to have no relation with oxidation of ammonia or loss of nitrogen.

The foregoing results prove that the ammonium salts are oxidised to nitrate by hydrogen peroxide and the oxidation is facilitated by addition of copper. Moreover, when the ammonium salt oxidation is greater, the loss of nitrogen is also found increased.

#### SUMMARY

The ammonium salts are oxidised to nitrate by hydrogen peroxide and nitrogen is lost in the process. The oxidation of ammonium salts is increased by the presence of copper. When the oxidation to nitrate is greater, the loss of nitrogen is also increased.

# VALUE OF COALS IN CROP PRODUCTION

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FROM extensive researches carried on for over twenty-five years in these laboratories it has been concluded that apart from the improvement in the physical condition and base-exchange capacity of the soil, the main function of organic matter is the fixation of atmospheric nitrogen and the preservation of soil or added nitrogen. The fixation of nitrogen can take place in the complete absence of micro-organisms and is increased by the absorption of sunlight or artificial light. We have studied all types of energy materials including coal, for fixing atmospheric nitrogen and protecting soil or added nitrogen.

In this communication, the results showing the beneficial effect of bituminous-coal and a mixture of wheat straw and small bits of 'Sahjan' wood (*Moringa pterygosperma*) in the yield of crops are recorded. In the case of coal the paddy seeds were sown immediately after the addition of bituminous coal on 19-7-1950; while in the case of straw and wood a time interval of three months for the fixation of atmospheric nitrogen was given and only wheat seeds were sown in October 1950.

The following results have been obtained:—

TABLE I. *Analysis of bituminous-coal*

Total carbon	..	..	..	..	77.36	per cent.
Total nitrogen	..	..	..	..	1.750	„
C: N ratio	..	..	..	..	44.21	

TABLE II. *Soil analysis of control plot*

Plot	Total carbon on dry basis %	Nitrogen on dry basis gram per cent.				C: N ratio
		Total	Ammoniacal	Nitric	Total available	
Control plot before sowing paddy ..	0.2212	0.0350	0.0144	0.0040	0.0184	6.3
Control plot after harvesting paddy	0.1550	0.0315	0.0083	0.0036	0.0119	4.9
Control plot after harvesting wheat	0.1617	0.0308	0.0068	0.0032	0.0100	5.2

TABLE III. *Soil analysis of plot treated with bituminous coal at the rate of 10 tons per acre*

Plot	Total carbon on dry basis %	Nitrogen on dry basis gram per cent.				C : N ratio
		Total	Ammoniacal	Nitric	Total available	
Treated with coal before sowing paddy ..	0.9147	0.0510	0.0151	0.0047	0.0198	17.9
Treated with coal after harvesting paddy ..	0.5872	0.0876	0.0280	0.0054	0.0334	6.7
Treated with coal after harvesting wheat ..	0.5094	0.0611	0.0062	0.0131	0.0193	8.3

TABLE IV. *Production of grain and straw of the paddy crop*

Plot	Production of grain in mds. per acre	Production of straw in mds. per acre
Control plot .. ..	7.09	25.60
Plot treated with coal ..	9.90	33.05

The percentage of increase of yield in the plot treated with coal as compared with the control plot are:—

In the grain .. ..	39.6
In the straw .. ..	28.7

TABLE V. *Production of grain and straw of the wheat crop*

Plot	Production of grain in mds. per acre	Production of straw in mds. per acre
Control plot .. ..	2.0	11.5
Plot treated with coal ..	4.3	10.9
Plot treated with straw and wood .. ..	4.2	10.6

In the case of wheat crop also the production of grain in the plot treated with coal and plot treated with straw and wood are more than double as

compared with the control plot. The straw produced in the control plot is however greatest.

#### SUMMARY

Bituminous-coal added at the rate of 10 tons per acre produces better paddy and wheat crops and in this no time interval between the addition of coal and the sowing of a crop is needed. There is a marked residual effect of coal, straw added at the rate of 10 tons per acre and about 10 tons of bits of wood 'Sahjan' (*Moringa pterygosperma*) practically containing the same amount of carbon compounds as the coal, produced an increase of wheat when there was a time interval of three months between the addition of the straw and wood and the sowing of wheat.

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## RETARDING INFLUENCE OF SOME LEGUMES ON NITROGEN LOSS IN SOILS

BY N. R. DHAR AND VIRENDRA SHARMA

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Received February 29, 1952

It has been established that light plays an important role in the ammonification, nitrification, denitrification, and fixation of atmospheric nitrogen. Dhar has emphasised that all the soil processes can take place in the complete absence of micro-organisms provided light and energy materials are available.

The process of nitrification has been found to be associated with nitrogen losses.

The following experiments have been performed to throw more light on the mechanism of loss of nitrogen from soils when nitrogenous compounds like ammonium sulphate and sodium nitrate are added to the soil and also to study the retarding influence of some legumes like *kudzu*, *sanai* and *clover* on such nitrogen loss:—

### EXPERIMENTAL

300 gm. of powdered and dried normal soil (after passing through 1 mm. sieve) was taken in some shallow enamelled dishes and ammonium sulphate and sodium nitrate (nitrogen content 0.01%) were added.

To another set of dishes containing the same amount of soil, were added amounts of the fresh plant materials (*kudzu*, *sanai*, *clover*) in the form of the whole plant (2% concentration) to ammonium sulphate and sodium nitrate (0.01% nitrogen content). Two sets of all the dishes of the same plant material were taken, one set exposed to sunlight and another kept in the dark. The mixtures were then thoroughly mixed. Samples were taken out from each dish and analysed for their initial total carbon and total nitrogen percentages. The original soil and the plant materials mixed were also analysed for the initial total carbon and total nitrogen percentages.

15% of distilled water was added to each dish and they were again mixed thoroughly. One set was kept exposed to sunlight uncovered while the other

was covered with black cloth. They were daily exposed to sunlight for about eight hours for a period of about three months.

To facilitate the oxidation of the nitrogenous salts added, the mixtures were stirred well and 10% of distilled water was added daily to the uncovered sets and on alternate days to the covered ones. The time of exposure and the mean temperature were recorded daily.

From time to time a portion of each mixture was sampled out and analysed carefully.

Total carbon and total nitrogen were estimated according to the method of Robinson, McLean and Williams. For total nitrogen the regular Kjeldahl method was modified to include nitrate and the standard salicylic acid method was followed.

The experimental results are given in the following tables:—

*Initial Estimations*

Substance used				% of total carbon	% of total nitrogen	C: N ratio
1.	Normal soil	..	..	0.4887	0.0496	9.86
2.	Kudzu (whole plant)	..	..	12.87	0.6999	18.38
3.	Sanai (whole plant)	..	..	14.02	0.8820	15.74
4.	Clover	..	..	18.80	0.9876	19.03

(a) Soil taken in all the dishes .. .. 300 gm.

(b) Concentration of the plant materials .. 2% of the soil

(c) Concentration of the artificials:

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> .. .. 0.01% of N<sub>2</sub>  
(actual wt. = 0.1414 gm.)

NaNO<sub>3</sub> .. .. 0.01% of N<sub>2</sub>  
(actual wt. = 0.1821 gm.)

TABLE I  
*Nitrogen loss with  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NaNO}_3$  in soil*

Conditions	EXPERIMENTS WITH $(\text{NH}_4)_2\text{SO}_4$				EXPERIMENTS WITH $\text{NaNO}_3$			
	300 gm. of soil + 0.1414 gm. of $(\text{NH}_4)_2\text{SO}_4$ (0.01% $\text{N}_2$ )				300 gm. of soil + 0.1821 gm. of $\text{NaNO}_3$ (0.01% $\text{N}_2$ )			
	Dates	Total carbon %	Total nitrogen %	Loss %	Dates	Total carbon %	Total nitrogen %	Loss %
Exposed ..	24-11-50	0.4902	0.0593	..	26-11-50	0.4898	0.0590	..
Covered ..	24-11-50	0.4902	0.0593	..	26-11-50	0.4898	0.0590	..
Exposed ..	25- 1-51	0.4900	0.0537	57.73	26- 1-51	0.4896	0.0566	25.42
Covered ..	25- 1-51	0.4900	0.0554	40.02	26- 1-51	0.4896	0.0572	19.15
Exposed ..	1- 3-51	0.4900	0.0511	84.59	2- 3-51	0.4898	0.0553	39.35
Covered ..	1- 3-51	0.4900	0.0533	61.85	2- 3-51	0.4898	0.0562	29.78



TABLE II  
Retarding effect of Kudzu (whole plant) on nitrogen loss with  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NaNO}_3$  in soil

Conditions	EXPERIMENTS WITH $(\text{NH}_4)_2\text{SO}_4$ AND Kudzu				EXPERIMENTS WITH $\text{NaNO}_3$ AND Kudzu			
	Dates	Total carbon %	Total nitrogen %	Loss %	Dates	Total carbon %	Total nitrogen %	Loss %
Exposed ..	27-11-50	0.6988	0.0739	..	27-11-50	0.6985	0.0737	..
Covered ..	27-11-50	0.6988	0.0739	..	27-11-50	0.6985	0.0737	..
Exposed ..	27- 1-51	0.6068	0.0714	25.0	27- 1-51	0.5999	0.0726	11.0
Covered ..	27- 1-51	0.6323	0.0725	14.0	27- 1-51	0.6263	0.0731	6.0
Exposed ..	3- 3-51	0.5723	0.0705	34.0	3- 3-51	0.5645	0.0720	17.0
Covered ..	3- 3-51	0.6101	0.0718	21.0	3- 3-51	0.6000	0.0726	11.0

TABLE III  
Retarding effect of Sanai (whole plant) on nitrogen loss with  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NaNO}_3$  in soil

Conditions	EXPERIMENTS WITH $(\text{NH}_4)_2\text{SO}_4$ AND Sanai				EXPERIMENTS WITH $\text{NaNO}_3$ AND Sanai			
	300 gm. of soil + 6 gm. of Sanai + 0.1414 gm. of $(\text{NH}_4)_2\text{SO}_4$ (0.01% $\text{N}_2$ )				300 gm. of soil + 6 gm. of Sanai + 0.1821 gm. of $\text{NaNO}_3$ (0.01% $\text{N}_2$ )			
	Dates	Total carbon %	Total nitrogen %	Loss %	Dates	Total carbon %	Total nitrogen %	Loss %
Exposed ..	29-11-50	0.7211	0.0759	..	29-11-50	0.7206	0.0757	..
Covered ..	29-11-50	0.7211	0.0759	..	29-11-50	0.7206	0.0757	..
Exposed ..	29- 1-51	0.6401	0.0732	27.0	29- 1-51	0.6337	0.0745	12.0
Covered ..	29- 1-51	0.6605	0.0742	17.0	29- 1-51	0.6491	0.0749	8.0
Exposed ..	5- 3-51	0.6128	0.0721	38.0	5- 3-51	0.6037	0.0738	19.0
Covered ..	5- 3-51	0.6493	0.0733	26.0	5- 3-51	0.6328	0.0743	14.0

TABLE IV  
Retarding effect of Clover (whole plant) on nitrogen loss with  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NaNO}_3$  in soil

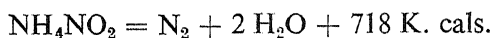
EXPERIMENTS WITH $(\text{NH}_4)_2\text{SO}_4$ AND CLOVER					EXPERIMENTS WITH $\text{NaNO}_3$ AND CLOVER					
Conditions	300 gm. of soil + 6 gm. of clover + 0.1414 gm. of $(\text{NH}_4)_2\text{SO}_4$ (0.01% $\text{N}_2$ )	Dates	Total carbon %	Total nitrogen %	Loss %	300 gm. of soil + 6 gm. of clover + 0.1821 gm. of $\text{NaNO}_3$ (0.01% $\text{N}_2$ )	Dates	Total carbon %	Total nitrogen %	Loss %
Exposed	.. 30-11-50	.. 30-11-50	0.8199	0.0782	..	.. 30-11-50	.. 30-11-50	0.8190	0.0781	..
Covered	.. 30-11-50	.. 30-11-50	0.8199	0.0782	..	.. 30-11-50	.. 30-11-50	0.8190	0.0781	..
Exposed	.. 30- 1-51	.. 30- 1-51	0.6899	0.0762	20.0	.. 30- 1-51	.. 30- 1-51	0.6769	0.0773	8.0
Covered	.. 30- 1-51	.. 30- 1-51	0.7201	0.0771	11.0	.. 30- 1-51	.. 30- 1-51	0.7159	0.0776	5.0
Exposed	.. 6- 3-51	.. 6- 3-51	0.6498	0.0755	27.0	.. 6- 3-51	.. 6- 3-51	0.6308	0.0768	13.0
Covered	.. 6- 3-51	.. 6- 3-51	0.6950	0.0766	16.0	.. 6- 3-51	.. 6- 3-51	0.6877	0.0772	9.0

## DISCUSSION

From the foregoing results it is clear that a large percentage of the nitrogen added to the soil in the form of ammonium sulphate and sodium nitrate is lost in about three months. It is very interesting to note that there is always a greater loss of nitrogen from the soil in the sets exposed to sunlight than in those kept covered with black cloth. It may thus be emphasised that the nitrification of these salts is much quicker in the uncovered dishes than in those which are kept covered.

With sodium nitrate, the loss of nitrogen is less than with ammonium sulphate.

The possible explanation for this nitrogen loss may be that at the first stage, during the nitrification taking place in the soil ammonium ion and the nitrite ions which are formed from ammonium ion or nitrate ion are present simultaneously. Ammonium nitrite being an unstable substance decomposes into free nitrogen gas and water. Thus gaseous nitrogen escapes in air from the fields and dishes causing the loss according to the equation:—



The ammonium salts are oxidised more in light than in the dark, and hence the formation and decomposition of ammonium nitrite becomes greater in light than in the dark. Thus, the loss of nitrogen is greater in the exposed sets than in the covered ones.

These results clearly indicate the possibility of the non-biological and thus photochemical decomposition of the nitrogenous compounds, which is accelerated by the sunlight in a marked manner. Had the nitrification and hence the nitrogen loss been bacterial alone, as is generally supposed to be, it would have been greater in the covered sets than in the exposed ones bacterial population is greater in the dark than in sunlight, which inactivates and kills micro-organisms.

The results show that when leguminous plants like *kudzu*, *sanai* and *clover* are added to the soil in addition to the fertilizers, there is a remarkable retardation in the nitrogen loss.

It appears that organic matter not only improves soil texture by adding colloids but also the carbonaceous matter added acts as an agent in the preservation of the nitrogenous compounds of the soil by behaving as a negative catalyst and enriches the soil by fixation of nitrogen due to the energy liberated in its oxidation.

C: N ratio of the initial mixtures is also greater than 10 in most of the cases. Due to this reason too intermediary nitrogen fixation may take place on one side which decreases the amount of nitrogen loss due to nitrification. This shows that C: N ratio also plays some part in the process of nitrogen loss in this way. But it should be clear that with intense sunshine and high nitrogen content, the photodecomposition of nitrogenous compounds in the process of nitrification may be more pronounced than this photochemical fixation of nitrogen in these cases.

It is also interesting to note that the order for the retarding effect on the nitrogen loss by these plants is the same as observed in case of nitrogen fixation by the direct addition of these plant materials all alone to the soil. It is, therefore, clear that the carbon oxidation and hence the nitrogen fixation or the nitrogen loss are correlated phenomena of the same order. The order for the retarding effect of these legumes is:

Clover → *Kudzu* → *Sanai*.

It is, therefore, clear from the above results that the manurial value of the artificial fertilizers is increased if they are mixed with these leguminous plants like *kudzu*, *sanai* and clover.

#### SUMMARY

1. It has been observed that when ammonium sulphate or sodium nitrate are added to the soil in dishes and exposed to sunlight, a loss of nitrogen takes place.
2. This loss of nitrogen is greater in exposed sets than in the covered ones.
3. With ammonium sulphate as fertilizer, the % of loss has been found greater than with sodium nitrate.
4. By mixing some legumes like *kudzu*, *sanai* and clover, it has been observed that the loss of nitrogen is checked. It is quite interesting that the order of this checking is just the same as that of the efficiencies of nitrogen fixation of all these legumes. The order is:

Clover — *Kudzu* — *Sanai*.

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THE NATIONAL ACADEMY OF SCIENCES (INDIA)

# SYMPOSIUM

ON THE

# CHEMISTRY OF HYDROUS OXIDES

1952

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VOLUME 21

SUPPLEMENT

SECTION A

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A symposium on the Chemistry of Hydrous Oxides was held on the occasion of the Annual Session of the National Academy of Sciences, India, at the Chemistry Lecture Theatre, Lucknow University, on the 9th February, 1952. The symposium was presided over by Professor N. R. Dhar, D. Sc. (London and Paris), F. R. I. C., F. N. I., F. N. A. Sc., I. E. S. (Retired), Head of the Chemistry Department and Director, Sheila Dhar Institute of Soil Science, University of Allahabad. The symposium was opened by Dr. S. Ghosh, D. Sc., F. N. A. Sc., Reader in Chemistry, University of Allahabad. In the opening remarks, the speaker referred briefly to the work carried on by him and his collaborators, in the Chemical Laboratories of the University of Allahabad, on the chemistry of Hydrous Oxides. The work on hydrous oxides has been carried mainly on the following lines :

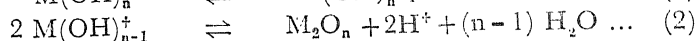
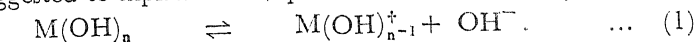
*Precipitation of Hydrous Oxides of heavy metals from their salt Solutions :* It has been observed that precipitation often occurs with an amount of alkali, which is less than the theoretically equivalent amount. Earlier workers in this direction, who happened to observe this fact ascribed this phenomenon to the formation of basic salts. Ghosh and coworkers have emphasised the role of adsorption in such precipitation phenomena and they have obtained sufficient data to support this viewpoint.

These authors have further shown the dependence of chemical properties of hydrous oxides on the conditions of precipitation, and have obtained samples having varying chemical activity, by the regulation of the concentration of alkali and the temperature of precipitation.

*Adsorption of Ions :* The adsorption studies with different samples of various hydroxides have definitely shown the importance of hydrogen ion concentration of the medium in which adsorption takes place. Adsorption of various ions and dyes—both acidic and basic—have been done and the data throw considerable light on the properties of hydrous oxides.

*Peptisation of Hydrous Oxides* : Studies on the colloidal behaviour of different hydrous oxides have been made, by the work on their peptisation, and investigations on the physical properties of the colloids so formed.

*Amphoteric behaviour of Hydrous Oxides* : The variation of the properties of hydrous oxides depend on their amphoteric character. The following mechanism has been suggested to explain the amphoteric behaviour of hydrous oxides :



Equation (1) shows the basic nature of the hydroxide of a  $n$ -valent metal  $M$ , since it liberates an  $OH^-$  ion. Often in weakly acidic hydroxides, it is difficult to conceive the liberation of a proton from the hydroxide itself. But we can understand the liberation of  $H^+$  ions from a positively charged body as shown in equation (2). The acid behaviour of such amphoteric hydroxides is thus explainable from this viewpoint. The mutual neutralisation of the acid and basic properties of the hydroxide results in the formation of an inert type of anhydrous oxide devoid of much chemical activity. Thus the variation of the properties of hydroxides, with the method of precipitation, can be understood by the proposed mechanism.

After the opening remarks, the following papers were read and discussed :

S. R. Gupta and S. Ghosh, Allahabad : Yellow Hydrous Ferric Oxide.

K. H. Gayer and A. B. Garrett, Ohio, U. S. A. : Equilibria of Antimonous Oxides (Rhombic) in dilute solutions of Hydrochloric Acid and Sodium Hydroxide at  $25^\circ C$ .

S. D. Jha, Delhi : Nature of Structural Flow in Sols.

G. S. Rao and S. N. Banerji, Sagar : The decomposition of Sodium Molybdate by Hydrochloric Acid and the effect of ageing on the system.

S. N. Tewari and S. Ghosh, Allahabad : Studies in the amphoteric nature of hydrated chromium oxide and the determination of its isoelectric point.

S. N. Tewari and S. Ghosh, Allahabad : Studies in the amphoteric nature of hydrated aluminium oxide and the determination of its isoelectric point.

S. N. Tewari, A. K. Dey and S. Ghosh, Allahabad : A note on the mechanism of ageing of Hydrous Oxides.

Among those who took part in the discussion were, Professor N. R. Dhar (Allahabad), Professor A. C. Chatterji (Lucknow) and Dr. K. S. Gururaja Doss (Kanpur). The symposium then closed with votes of thanks to the chair and to the authors who contributed papers and also to those who took part in the discussions.

# YELLOW HYDROUS FERRIC OXIDE

BY S. R. GUPTA AND S. GHOSH.

*Chemical Laboratory, University of Allahabad.*

## ABSTRACT.

In a number of publications Ghosh and coworkers have investigated the variation in the properties of the hydrous oxides of Iron<sup>1</sup>, Chromium<sup>2</sup>, Aluminium<sup>3</sup> and Tin<sup>4</sup>, when they are precipitated from their soluble salts under various conditions. The present paper deals with the nature of a variety of hydrous ferric oxide obtained from ferric chloride solution by the addition of very insufficient quantities of caustic soda solution; the precipitation being enhanced by potassium sulphate solution. The hydrous oxide thus obtained remarkably differ in property both physical and chemical.

## INTRODUCTION.

Britton<sup>5</sup> has observed from the potentiometric titrations that metallic hydroxides are precipitated with alkali hydroxides even with a smaller amount than the equivalent amount. He opined that in the case of the precipitation of several hydrous oxides with deficient alkali results in the formation of a basic salt. Similar contentions are held by Heubel<sup>6</sup>, Dechamps<sup>7</sup>, Pickering<sup>8</sup>, Margnerite Quintin<sup>9</sup>, Halder<sup>10</sup> and many others. But the work of Ghosh and coworkers, on the precipitation of several hydrous oxides corroborates the observation of Britton and others, in as much as that deficient amount of alkali effect complete precipitation but they have been not able to lend a total support to the formation of basic salt in explaining such phenomena. Their work shows that the specific adsorption of an anion present in the solution results in the generation of free alkali, which in its turn completes the precipitation in addition to the alkali added. It has been further shown that the adsorption of the anion is more prominent when alkali added is in deficient quantity and that it decreases when either the equivalent amount or excess of alkali is added to the metal salt solutions. In the case of precipitation of the hydrated oxides of Tin, Iron, Aluminium and Chromium the amount of alkali required for complete precipitation is always smaller than the equivalent amount and this difference is more remarkable for concentrated solutions of metal salts than for dilute ones, where the amount of alkali to precipitate approaches the theoretical value; obviously the hydrolysis is favoured for dilute solutions and this observation proves beyond doubt that adsorption plays a significant role in the precipitation of the hydrated oxides of these metals. They arrived at similar conclusions by precipitating hydrous oxides at higher temperatures.

These observations on precipitation of hydrous oxides were, however, limited to the concentrations of the alkali added near about the complete precipitation from

their soluble salt solutions. In this paper, therefore, changes that are brought about when alkali is added in different amounts (much below the amount needed for complete precipitation) to the soluble salt solution has been investigated. Now some of the preliminary experiments are described below :

#### EXPERIMENTAL.

It is well known that a colloidal solution of ferric hydroxide can be obtained by the addition of an alkali solution to a soluble ferric salt solution when the alkali is very small in amount. The colloidal hydroxide thus formed remains in peptised condition because of a large excess of the stabilising ferric ions, and could not be precipitated by univalent electrolytes like sodium chloride, but the same can be achieved by the addition of potassium sulphate or other sodium or potassium salt of a polyvalent anion.

The experiment was performed by taking 10 c.c. of  $\frac{M}{10}$  ferric chloride solution in different test tubes and 3 c.c. of  $\frac{M}{2}$  potassium sulphate with varying amounts of 0.3 N caustic soda made up to 10 c.c. The two were then mixed and 5 c.c. of this mixture was pipetted out at intervals through glass wool and centrifuged for one minute at 1,000 revolutions per minute (The effect of centrifuge on precipitation of colloid is negligible) 2 c.c. of the supernatant liquid was analysed for iron content by usual the volumetric method employing potassium dichromate and using N—phenyl anthranilic acid as internal indicator.

In the course of the performance of the above experiments a significant observation is made that there is an immediate precipitation of hydrous ferric oxide orange brown in colour when the two solutions are mixed. After this brown oxide has been precipitated, further precipitation takes place of the hydrous oxide which is remarkably slow and its colour varies from orange yellow to whitish yellow according to the conditions of the experiment ; this being more whitish yellow when the precipitation is carried out with smaller amount of alkali. It is further noted that in the separation of this yellow product there is a time lag which becomes shorter with increase in alkali concentration and also by increasing the concentration of potassium sulphate solution ; the former being however more significant. It was therefore thought necessary to investigate the rate of such precipitation. This was done by the analysis of the supernatant liquid for the iron content at different intervals of time as described previously. The results obtained are given in the following tables and the graphical representation of the precipitation of the precipitation are given in curves given in Fig. Nos. I and II. In the first and second tables the concentration of potassium sulphate is kept constant while that of caustic soda is varied.

# YELLOW HYDROUS FERRIC OXIDE

Table I.

Kinetics of precipitation at room temperature.

Volume of 0.0955 M Fe Cl<sub>3</sub> solution = 10 c. c.

Volume of  $\frac{M}{2}$  K<sub>2</sub>SO<sub>4</sub> 4 c.c. + alkali + water = 10 c.c.

Total Volume = 20 c.c.

2 c.c. of the supernatant liquid taken for iron estimation in each case, and  
titrated against  $\frac{N}{20}$  K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

Time	Vol. of N 20 K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> with 2 c.c. 0.298M NaOH	Vol. of N 20 K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> with 4 c.c. 0.298M NaOH	Vol. of N 20 K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> with 5 c.c. 0.298M NaOH	Vol. of N 20 K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> with 6 c.c. 0.298M NaOH
0 min.	1.91 c.c.	1.91 c.c.	1.91 c.c.	1.91 c.c.
5 min.	1.81 c.c.	1.63 c.c.	1.32 c.c.	0.85 c.c.
10 min.	1.81 c.c.	1.61 c.c.	1.30 c.c.	0.78 c.c.
20 min.	1.81 c.c.	1.40 c.c.	1.22 c.c.	0.78 c.c.
25 min.	1.81 c.c.	1.33 c.c.	1.19 c.c.	0.78 c.c.
40 min.	1.78 c.c.	1.22 c.c.	1.13 c.c.	0.78 c.c.
60 min.	1.68 c.c.	1.12 c.c.	1.04 c.c.	0.71 c.c.
80 min.	1.67 c.c.	1.10 c.c.	0.95 c.c.	0.65 c.c.
100 min.	1.67 c.c.	1.04 c.c.	0.89 c.c.	0.62 c.c.
115 min.	1.67 c.c.	1.04 c.c.	0.85 c.c.	0.57 c.c.
24 hours	1.56 c.c.	1.00 c.c.	0.75 c.c.	0.56 c.c.

Table II.

Kinetics of precipitation at room temperature.

Volume of 0.09975 M Fe Cl<sub>3</sub> solution = 10 c.c.

Volume of  $\frac{M}{2}$  K<sub>2</sub>SO<sub>4</sub> 3 c.c. + alkali + water = 10 c.c.

Total Volume = 20 c.c.

2 c.c. of the supernatant liquid taken for iron estimation each time, and  
titrated against  $\frac{N}{20}$  K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

Time	Vol. of M/20 K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> with 2 c.c. NaOH (0.298 M)	Vol. of M/20 K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> with 4 c.c. NaOH (0.298) M	Vol. of M/20 K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> with 6 c.c. NaOH (0.298) M
0 min.	1.95 c.c.	1.95 c.c.	1.95 c.c.
5 min.	1.85 c.c.	1.50 c.c.	0.77 c.c.
10 min.	1.85 c.c.	1.42 c.c.	0.72 c.c.
15 min.	1.85 c.c.	1.42 c.c.	0.72 c.c.
20 min.	1.85 c.c.	1.37 c.c.	0.71 c.c.
35 min.	1.80 c.c.	1.22 c.c.	0.70 c.c.
50 min.	1.73 c.c.	1.16 c.c.	0.69 c.c.
75 min.	1.70 c.c.	1.07 c.c.	0.65 c.c.
95 min.	1.57 c.c.	1.07 c.c.	0.62 c.c.
110 min.	1.57 c.c.	1.05 c.c.	0.62 c.c.
24 hours.	1.56 c.c.	1.00 c.c.	0.59 c.c.

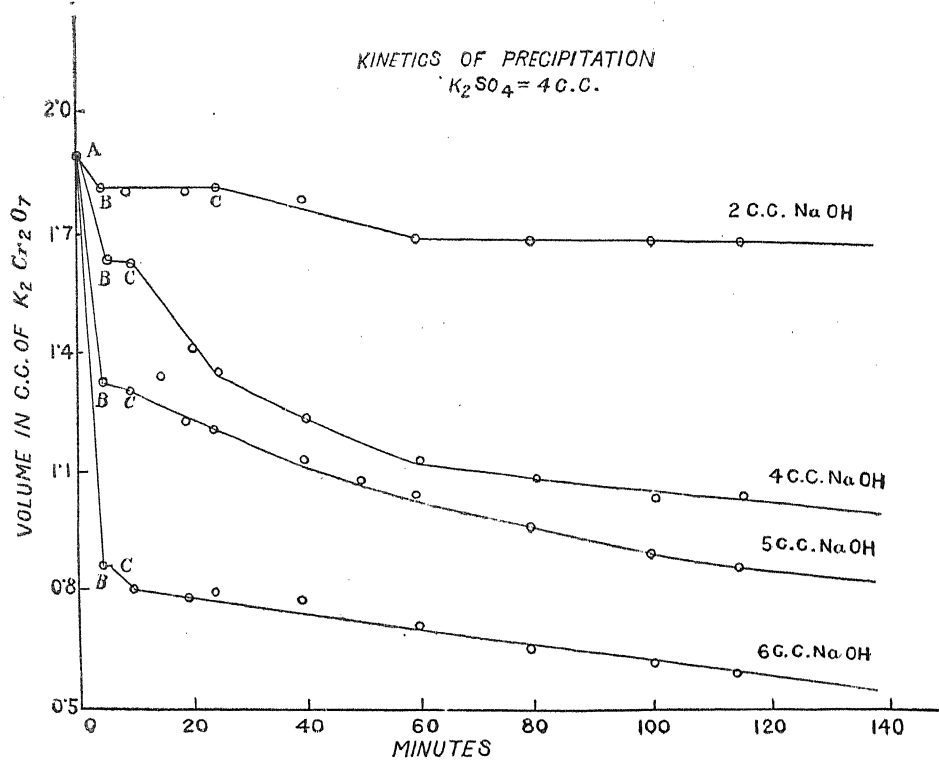


FIG No. I

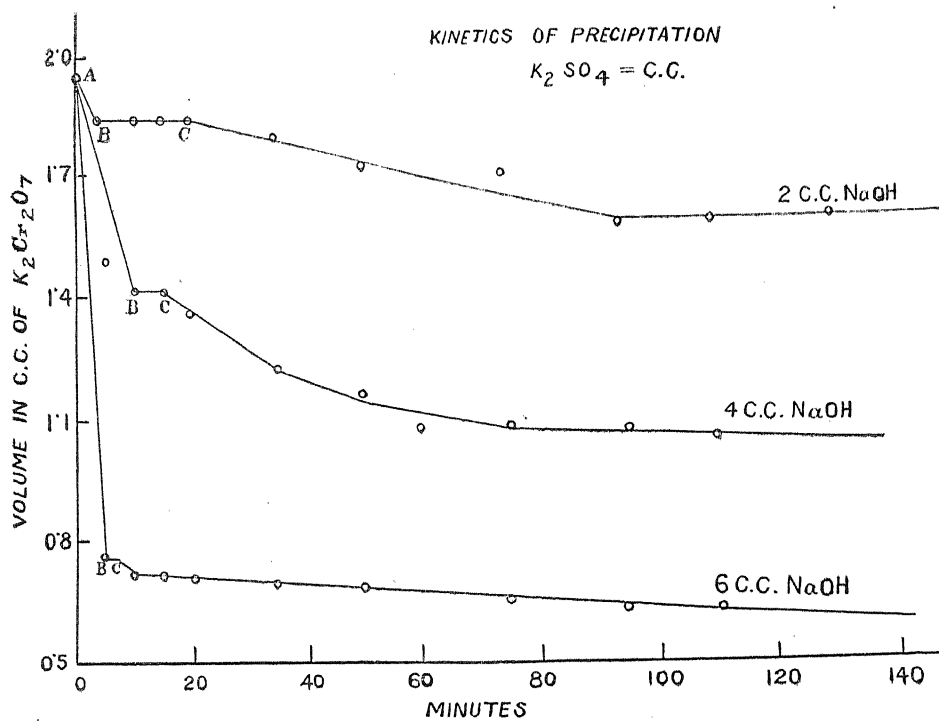


FIG No. II

The precipitation curves in fig. I and II have three definite portions ; the first and the steep portion AB represents the immediate formation of the brown hydrous oxide. The second horizontal portion BC represents the time lag and the third portion representing the slow precipitation indicates the formation of the yellow hydrated oxide. The changes in the steep, horizontal and curved portion clearly indicates the effect of alkali concentration on the formation of brown hydrous oxide, the time lag and formation of yellow hydrous oxide.

We have also carried out the analysis of both brown and yellow varieties of hydrous ferric oxide as obtained in these experiments. As the anions entrained by hydrous oxides are liable to differ by washing the precipitates, the analysis of the precipitated material has been effected indirectly in the following way.

The iron content in the supernatant liquid were estimated immediately first after the formation of brown precipitate and also after the formation of yellow precipitate which reaches to complete precipitation by standing for about 10 hours. The chloride and sulphate contents were similarly estimated. From these results it is possible now to calculate the amount of iron and associated anions present in the brown or yellow varieties and the results are given below in the following tables :—

Table IV.

Volume of 0.099 M Fe Cl<sub>3</sub> Solution=100 c.c.

Volume of 20 c.c. 0.491M K<sub>2</sub>SO<sub>4</sub> + alkali + water=100 c.c.

Total volume=200 c.c.

Amount of NaOH. 0.298 N.	Amount of iron in gm. atoms.			Precipitated iron in gm. atoms.		Total pre-cipitated iron in gm. atoms.	Theoretically precipitated iron in gm. atoms.
	Original	After Brown	After Yellow	Brown	Yellow		
10 c.c.	0.0099	0.00975	0.00915	0.00015	0.00060	0.00075	0.000993
20 c.c.	0.0099	0.00905	0.00770	0.00085	0.00135	0.00220	0.001986
30 c.c.	0.0099	0.00795	0.00665	0.00195	0.00130	0.00325	0.002979
40 c.c.	0.0099	0.00680	0.00485	0.00310	0.00195	0.00505	0.003972
50 c.c.	0.0099	0.00540	0.00420	0.00450	0.00120	0.00570	0.004965
70 c.c.	0.0099	0.00260	0.00155	0.00730	0.00105	0.00835	0.006851
80 c.c.	0.0099	0.00120	0.00065	0.00870	0.00055	0.00925	0.007944

Table V.

Volume of 0.099 M Fe Cl<sub>3</sub> Solution=100 c.c.

Volume of 20 c.c. 0.491 M K<sub>2</sub>SO<sub>4</sub> + alkali + water=100 c.c.

Total Volume=200 c.c.



Amount of NaOH 0.298 N.	Amount of Sulphate in gm. ions.		Amount of sulphate associated with in gm. ions.		
	Original	After Brown	After Yellow	Brown	Yellow
10 c.c.	0.00984	0.00961	0.00961	0.00023	Nil
20 c.c.	0.00984	0.00937	0.00917	0.00047	0.00020
30 c.c.	0.00984	0.00915	0.00893	0.00069	0.00022
40 c.c.	0.00984	0.00909	0.00854	0.00075	0.00055
50 c.c.	0.00984	0.00902	0.00805	0.00082	0.00097
70 c.c.	0.00984	0.00770	0.00751	0.00214	0.00019

Table VI.

Volume of 0.099 M  $\text{FeCl}_3$  Solution = 100 c.c.

Volume of 20 c.c. 0.491 M  $\text{K}_2\text{SO}_4$  + alkali + water = 100 c.c.

Total Volume = 200 c.c.

Amount of NaOH 0.298 N.	Amount of chloride in gm. atoms.		Amount of Chloride associated with in gm. atoms.		
	Original	After Brown	After Yellow	Brown	Yellow
10 c.c.	0.02977	0.02893	0.02893	0.00084	Nil
20 c.c.	0.02977	0.02893	0.02893	0.00084	Nil
30 c.c.	0.02977	0.02893	0.02893	0.00084	Nil
40 c.c.	0.02977	0.02893	0.02893	0.00084	Nil
50 c.c.	0.02977	0.02893	0.02893	0.00084	Nil
60 c.c.	0.02977	0.02893	0.02893	0.00084	Nil
70 c.c.	0.02977	0.02893	0.02893	0.00084	Nil
80 c.c.	0.02977	0.02893	0.02893	0.00084	Nil

The results in the above tables conclusively prove that the amount of anions associated with the iron present as brown hydrous oxide is significantly large when compared with those associated with yellow variety so much so that the chloride content is nil for the yellow hydrous oxide.

It is further noted that when caustic soda is added in different amounts to a ferric chloride solution in the presence of potassium sulphate a brown precipitate is obtained immediately which is more yellowish than reddish as is obtained when ferric hydroxide is precipitated by the addition of an excess of ammonium hydroxide or caustic soda solution to a ferric salt. This hydrous oxide is associated with a large amount of anions both chloride and sulphate. The amount produced of this hydrous oxide increases for the increasing amount of alkali and the amount of anions associated decreases.

The yellow hydrous oxide is found to be associated with no chloride but is associated with some sulphate radicals, which increases with the increasing amount of yellow product formed, which is maximum when about half of the quantity of caustic soda is added for complete precipitation as ferric hydroxide. The formation of this yellow hydrous oxide becomes less in proportion to the brown hydrous oxide formed with increasing amount of alkali added so much so that when 90% of the alkali is added for completely precipitating the ferric salt as ferric hydroxide no yellow product is formed. It also appears from these data that the adsorptive capacity for anions is smaller for the yellow hydrous ferric oxide than for the brown one. These results further confirm that no insoluble basic salt of iron is precipitated, as specially the yellow hydrous oxide obtained by one c.c. of alkali does not contain any chloride or sulphate intrained in it.

It will be of interest now to consider that the two varieties of hydrous ferric oxide are described in literature. D. Tommasi<sup>11</sup> has classified them as yellow and red or brown, which are isomeric or allotropic forms of one another. The members of the red series are produced by precipitating a ferric salt with an alkali which is reddish brown and amorphous on its immediate formation. It however quickly ages losing its chemical reactivity and adsorptive capacity which is hastened by boiling or when left in a dilute alkali solution.<sup>12</sup> With the progress of ageing, the hydrous oxide becomes crystalline and shows on X-ray analysis the structure of ferric hydroxide which is brick red in colour.

Tommasi<sup>13</sup> first recognised the yellow series of hydrous iron oxide which he obtained by oxidising hydrated ferrous carbonate. J. Bohn,<sup>14</sup> Albrecht,<sup>15</sup> Bodiush and co-workers<sup>16</sup> and several others have described the formation of this yellow hydrous ferric oxide better known as  $\gamma$  ferric oxide from the oxidation of hydrated ferrous oxide in the presence of potassium iodate, chlorate, sodium azide pyridine, etc. Weiser and Milligan,<sup>18</sup> however, also reported a yellow form of hydrated ferric oxide obtained from boiling solutions of dilute ferric chloride. These authors consider their yellow variety different from that described by Tommasi and others and have claimed to prepare a new modification or  $\beta$  hydrated ferric oxide.

The yellow hydrous oxide now obtained by us, shows many similarities with that described by Tommasi and the others. Thus it has very little catalytic activity in the decomposition of hydrogen peroxide. This yellow hydrous oxide hardly decomposes 5% of the hydrogen peroxide in one hour as estimated by potassium permanganate solution, whilst a brown hydrous oxide of iron precipitated by an equivalent amount of an alkali and aged for a day decomposes the same hydrogen peroxide more than 30% within the same time. The yellow hydrous oxide is also sparingly soluble in acetic acid whilst the brown modification dissolves to a great extent. As will be seen from the table given below:

Yellow hydrated ferric oxide prepared by 1 c.c. 0.3 N NaOH + 2 c.c. M/2 potassium sulphate + 10 c.c.  $\frac{M}{10}$  ferric chloride and the brown by adding 10 c.c. 0.3 N NaOH to 10 c.c.  $\frac{M}{10}$  ferric chloride solution.

The two equally aged samples were kept overnight in 100 c.c. 0.25N acetic acid and the iron in the solution was estimated.

Sample.	Amount of Iron.
Yellow	0.0001 gm. atom
Brown	0.0104 „ „

The yellow hydrous ferric oxide prepared by us on warming to about 150°C changes into a red modification known as  $\gamma$  ferric oxide, on hydrolysis effected by boiling in water, or addition of a dilute alkali or by grinding it tends to change to the same red modification the  $\gamma$  ferric oxide; further it dissolves completely in a strong alkali lye to form a colourless solution; the brown hydrous oxide which has aged for a couple of days refuses to do so.

These properties therefore show that the yellow hydrous ferric oxide obtained here is similar to that described by Tommasi. More work is in progress specially because the yellow product is of great commercial importance. It is manufactured and marketed under the name "Siderac" and as early as 1948 C. W. Voigt<sup>17</sup> prepared it by the oxidation of a ferrous salt formed directly by the action of iron filings and sulphuric acid on commercial scale.

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THE EQUILIBRIA OF ANTIMONOUS OXIDE (RHOMBIC) IN DILUTE  
SOLUTIONS OF HYDROCHLORIC ACID AND SODIUM  
HYDROXIDE AT 25°C.

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[Communicated by Dr. A. K. Dey.]

The purpose of this investigation was to obtain data on the equilibria of antimonous oxide in dilute hydrochloric acid and sodium hydroxide solutions. Previous work on antimonous oxide is incomplete in regard to solubility and equilibria values. The earliest reported work on the reactions of antimony was made by A. Terriel<sup>1</sup> who prepared sodium antimonite and studied some of its properties. H. Schulze<sup>2</sup> determined the solubility of antimony trioxide in water at 15° and 100° and found them to be  $5.5 \times 10^{-5}$  and  $3.4 \times 10^{-4}$  moles per 1000 grams of water respectively. R. Schuhmann<sup>3</sup> measured the solubility of antimony trioxide (probably the rhombic form) in several solutions of various concentrations of perchloric acid; and found a fairly constant value for the ratio of hydrogen ion concentration to antimony concentration, which led him to conclude that the  $\text{SbO}^+$  ion exists in acid solutions.

PROCEDURE.

The general procedure was similar to that of Garrett and Heiks<sup>4</sup>.

*Water.* Triple distilled water was used. It was boiled to free it from dissolved gases; then it was stored under nitrogen.

*Antimony Trichloride.* Baker and Adamson Reagent Antimony Trichloride was used to prepare the rhombic antimonous oxide.

*Antimony Metal.* Baker and Adamson Reagent Antimony was used to prepare the colorimetric standards.

*Sodium Carbonate.* Mallinkrodt's Anhydrous Analytical Reagent was used to precipitate the oxide.

*Hydrochloric Acid.* Standard solutions for analysis and for the solubility measurements were prepared from C. P. Hydrochloric Acid and standardized gravimetrically.

*Rhodamine B.* Eastman Kodak practical grade was used to prepare the 0.2% water solution.

*Rhombic Antimonous Oxide.* The antimonous oxide was prepared in an atmosphere of nitrogen. To a solution containing thirty grams of antimony trichloride per liter of water was added a saturated solution of sodium carbonate to

precipitate the antimony oxide. The oxide was then washed with triple-distilled, boiled water until free of chloride and sodium ions. Fifteen one-liter washings sufficed. The identity of the rhombic form was obtained by X-ray analysis.\*

*Equilibration.* Two 180 ml-samples of the equilibrating mixture, contained in 200 ml-round bottom flasks, were prepared at each concentration of alkali or acid. One sample was agitated in a thermostat at 35° for a period of five to seven days, then transferred to a thermostat at 25° ± 0.02°C for an additional agitation period of seven days. The other one of each pair was placed directly in the 25° thermostat and agitated for seven days. By this means, equilibrium was approached from supersaturation and undersaturation. Both values were found to check within experimental limits.

*Sedimentation.* After the completion of the agitation period, the flasks were clamped in an upright position in the 25° thermostat, and the oxide allowed to settle for seven days.

*Filtration.* The flasks were opened and contents removed under an atmosphere of nitrogen through a covered, sintered glass funnel, and into a glass stoppered bottle.

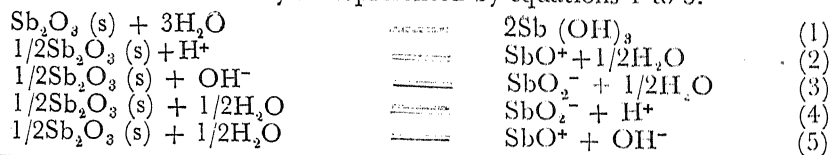
*Measurement of Hydrogen Ion Concentration.* The pH values of the equilibrated samples were obtained by using a Beckman portable pH meter. The meter was calibrated with potassium acid phthalate sodium hydroxide buffer at pH 4, and with boric acid-sodium hydroxide buffer at pH 10.

*Analysis of Antimony.* The antimony analysis on the equilibrated samples was made with a Lumetron spectrophotometer using rhodamine B to produce the colored complex. The procedure for analysis was a modification of that described by T. H. Maren<sup>5</sup>.

The analyses were reproducible at ± 3%.

The data are collected in Tables I and II and are shown graphically in Figure 1. The rhombic form of antimony oxide was used throughout. It is reported to be unstable at room temperature, but apparently the rhombic modification is formed on precipitation and changes over to the cubic only very slowly. No evidence of the cubic form was found in any of our samples. Since the rhombic form is the less stable form at room temperature, it will have a higher solubility than the cubic form.

In general, we can assume that the equilibria of antimony trioxide in neutral, acidic and basic solutions may be represented by equations 1 to 5.



\*We are indebted to Dr. D. A. Vaughan of the Battelle Memorial Institute for the X-ray analysis of these samples.

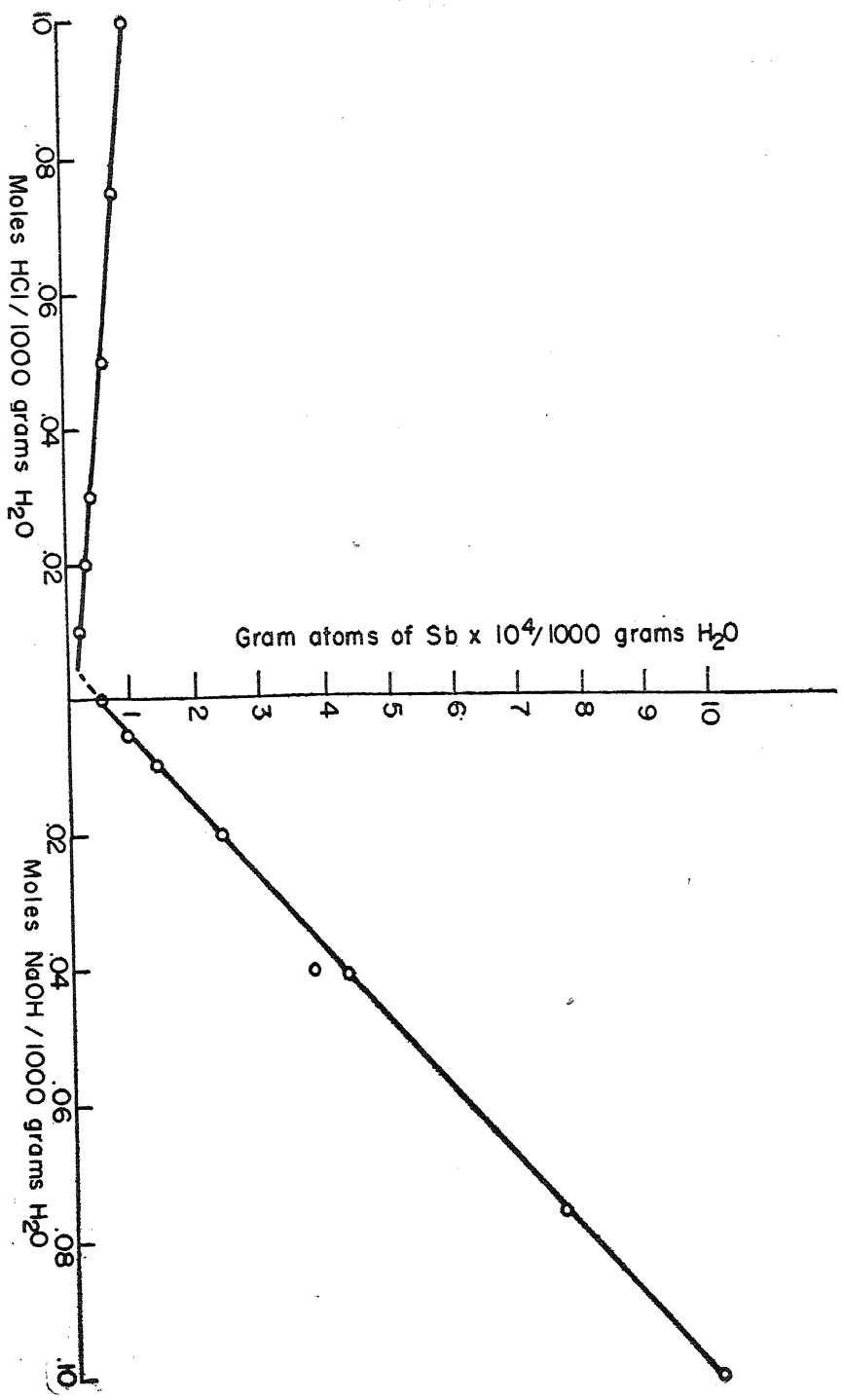
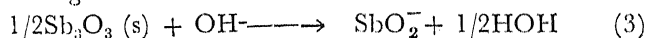


Fig. 1. SOLUBILITY OF  $\text{Sb}_2\text{O}_3$  (in gram atoms Sb) IN DILUTE ACID AND BASE

*The Solubility of Rhombic Antimonous Oxide in Water.* The solubility of antimonous oxide in water was found to be  $5.2 \times 10^{-5} \pm 1 \times 10^{-5}$  gram atoms of Sb per 1000 gram of water from an average of five determinations ranging from  $5.6 \times 10^{-5}$  to  $5.0 \times 10^{-5}$ . It was also found, from extrapolation (large scale) of the solubility of antimony oxide in alkaline solutions, to  $6.5 \times 10^{-5} \approx 10^{-5}$ . An average of the values is probably the most responsible value giving  $5.8 \times 10^{-5}$  gram atoms of antimony (Sb) per 1000 grams of water or  $2.9 \times 10^{-5}$  moles of  $\text{Sb}_2\text{O}_3$  per 1000 grams of water.

*The Equilibria in Basic Solutions.* The constancy of the values of  $K_3$  is evidence that the reaction indicated by Equation (3) accounts for the solubility of antimony oxide over this range of concentration of alkali.



$$\text{The equilibrium constant } K_3 = \frac{m\text{SbO}_2^- \cdot \gamma\text{SbO}_2^-}{m\text{OH}^- \cdot \gamma\text{OH}^-}$$

The ratio  $\frac{\gamma\text{SbO}_2^-}{\gamma\text{OH}^-}$  can be assumed to be unity over the concentration range studied. The value of  $m\text{SbO} =$  total antimony - undissociated antimony hydroxide. Since antimony hydroxide is a weak acid the undissociated antimony hydroxide can be determined by extrapolating the solubility curve for antimony oxide in base to  $m\text{OH}^- = 0$ ; this is the water solubility value which is determined to be  $5.8 \times 10^{-5}$ . The value of  $K_3$  is  $8.8 \times 10^{-3} \pm 1.0 \times 10^{-3}$  and  $\Delta F^\circ = 2800$  cal.

Further evidence for the monobasic character of the ions comes from the work of Terrell<sup>1</sup> who isolated sodium antimonite,  $\text{NaSbO}_2$ . There is no indication of the type of polymer formation found in the arsenious oxide-alkali system studied by Garrett, Holmes and Laube<sup>6</sup>.

Table I.

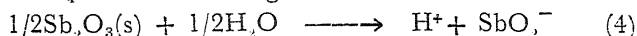
Solubility of Rhombic  $\text{Sb}_2\text{O}_3$  in NaOH Solutions at 25°.

Initial Moles NaOH/1000 grams $\text{H}_2\text{O}$	Gram Atoms of Sb/1000 grams $\text{H}_2\text{O}$	$K_3$
0.000	$5.8 \times 10^{-5}$	
0.00505	$9.8 \times 10^{-5}$	$7.9 \times 10^{-3}$
0.0101	$14.8 \times 10^{-5}$	8.9
0.0202	$23.8 \times 10^{-5}$	8.9
0.0404	$42.8 \times 10^{-5}$	9.2
0.0400	$37.8 \times 10^{-5}$	8.0
0.0749	$75.8 \times 10^{-5}$	9.3
0.0998	$99.8 \times 10^{-5}$	9.4
		Ave. $8.8 \times 10^{-3}$

Table II.  
Solubility Rhombic  $\text{Sb}_2\text{O}_3$  in  $\text{HCl}$  Solutions at  $25^\circ\text{C}$

Initial Moles $\text{HCl}/1000$ grams $\text{H}_2\text{O}$	Gram atoms of $\text{Sb}/1000$ grams $\text{H}_2\text{O}$	Moles $\text{H}^+/1000$ grams $\text{H}_2\text{O}$ from pH values	$K_2$
0.005	$2.1 \times 10^{-5}$	$5.2 \times 10^{-3}$	
0.010	2.6	$1.0 \times 10^{-2}$	$6.0 \times 10^{-4}$
0.020	3.4	$2.2 \times 10^{-2}$	7.0
0.030	4.5	$3.1 \times 10^{-2}$	8.3
0.050	6.1	$5.8 \times 10^{-2}$	8.2
0.075	8.2	$6.9 \times 10^{-2}$	8.3
0.100	10.2	$1.3 \times 10^{-1}$	8.2
			Ave. $7.7 \times 10^{-4}$

Using the value for  $K_3$  and the ion product of water,  $K_w$  the acid dissociation constant  $K_4$  for the following reaction was calculated:

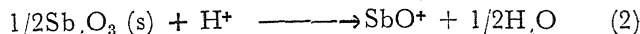


$$K_4 = \frac{m\text{SbO}_2^- \cdot \gamma\text{SbO}_2^-}{m\text{H}^+ \cdot \gamma\text{H}^+} = K_w K_3$$

$$K_4 = 8.8 \times 10^{-17}$$

$$\Delta F^\circ = 22,000 \text{ calories.}$$

*Equilibria in acid solution.* That the solubility of antimony trioxide in dilute hydrochloric acid solution can be accounted for by the reaction:



can be shown by the constancy of the values of  $K_2$ . Similar conclusions were drawn by Schuhmann<sup>3</sup> from the solubility of antimony trioxide in perchloric acid.

Using the data of Table II the equilibrium constant  $K_2$  for the above reaction was calculated:

$$K_2 = \frac{m\text{SbO}^+ \cdot \gamma\text{SbO}^+}{m\text{H}^+ \cdot \gamma\text{H}^+} = 7.7 \times 10^{-4}$$

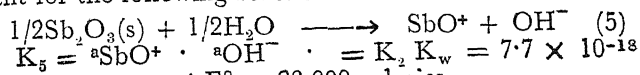
$$\Delta F^\circ = 4,300 \text{ calories.}$$

The ratio of  $\frac{\gamma\text{SbO}^+}{\gamma\text{OH}^-}$  can be assumed to be unity over the concentration range studied. The value for  $m\text{SbO}^+$  is obtained from the relationship:

$$m\text{SbO}^+ = \text{Total antimony concentration} - \text{the undissociated (antimony hydroxide)}$$

The value of undissociated hydroxide is found to be  $2 \times 10^{-5}$  from an extrapolation of the solubility in acid solution to  $m\text{HCl} = 0$ . The above value of  $K_2$  agrees well with that obtained by Schuhmann<sup>3</sup> ( $9.38 \times 10^{-4}$ ) using perchloric acid.

Using the above value for  $K_2$  and  $K_w$ , the ion constant for water,  $K_5$  the equilibrium constant for the following reaction can be obtained:



$$K_5 = \frac{m\text{SbO}^+ \cdot m\text{OH}^-}{m\text{H}^+} = K_2 K_w = 7.7 \times 10^{-18}$$

$$\Delta F^\circ = 23,000 \text{ calories.}$$



The above values agree with the values of  $1 \times 10^{-17}$  calculated by Latimer from form energy values.

#### SUMMARY.

The solubility of antimonous oxide has been determined in water and in dilute solutions of sodium hydroxide and hydrochloric acid. The equilibria in sodium hydroxide and in hydrochloric acid solutions indicate that the antimony is present in both cases as a monovalent ion. Values of the solubility of antimony oxide in water and for the acid and base constants of antimony trioxide have been obtained.

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## NATURE OF 'STRUCTURAL FLOW' IN SOLS

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[Communicated by Dr. A. K. Dey.]

### ABSTRACT

In this paper the ageing of hydrated ferric oxide and vanadium pentoxide sols has been investigated with respect to changes in viscosity at different shearing forces. The results have been discussed in the light of X-ray data of various sol systems.

In a number of communications Ghosh and co-workers (1) have reported the development of some 'loose-structure' in the case of different sols on ageing and dialysis. The development of this structure, before these investigations were undertaken by Ghosh, was ascribed by Dhar and Prakash (2) due to an increase in the hydration of the sol particles and resulting in an increase in the viscosity of sols. In this paper light has been thrown to elucidate the nature of this 'loose structure' as predicted by Ghosh. The phenomena of ageing of sols has been studied in case of some sols and the results interpreted in the light of modern X-ray analysis of sols. The study of ageing of sols throws light into the nature and structure of the sol particles.

Debye and Sherrer investigated from the X-ray picture of colloidal gold that the particles in the case of gold sols have the ordinary crystalline arrangement of gold of the face-centred cube. Weiser and Milligan (3) have studied the X-ray diagrams of ferric oxide on ageing, and densitometer curves from X-ray negatives obtained at different intervals show that as more and more period elapses, there is a tendency of crystallization. The growth of crystal takes place rather slowly at room temperature, but if the sol is allowed to age at higher temperature, then the appearance of crystals takes place rapidly.

In this paper the relative viscosity of the sols as given by the equation :—

$$\frac{\eta_s}{\eta_w} = \frac{\frac{1}{t_1} - \frac{1}{t_2}}{\frac{1}{t_1} + \frac{1}{t_2}}$$

Where  $\eta_s$  is the viscosity of the sol at a definite temperature and pressure.  $\eta_w$  is the viscosity of water under the same conditions,  $t_1$  and  $t_2$  represent the time of flow downwards and upwards the tube for water and  $t_1'$  and  $t_2'$  are the corresponding times for the sols. The experimental details of the apparatus used for measuring structural flow are as given by Ayub and Ghosh (4).

Sols of ferric oxide were prepared by precipitating ferric chloride as ferric hydroxide by the addition of ammonia. Ammonium chloride and the excess of ammonia were removed by continuous washing till the precipitate showed signs of peptization. Sample A was prepared by taking the washed precipitate and adding a few drops of dilute hydrochloric acid. Sample B was obtained by using a few drops of acetic acid as peptizing agent. The sols were dialyzed in cold and stored in pyrex bottles. The relative value of viscosity were determined at 20, 25 and 30 cms. of water column at a temperature of 30°C.

Table I.

Conc. of Sol A=13.98g/l of Solid  
matter.  
Conc. of Cl<sup>-</sup> ion=0.1,45g/l

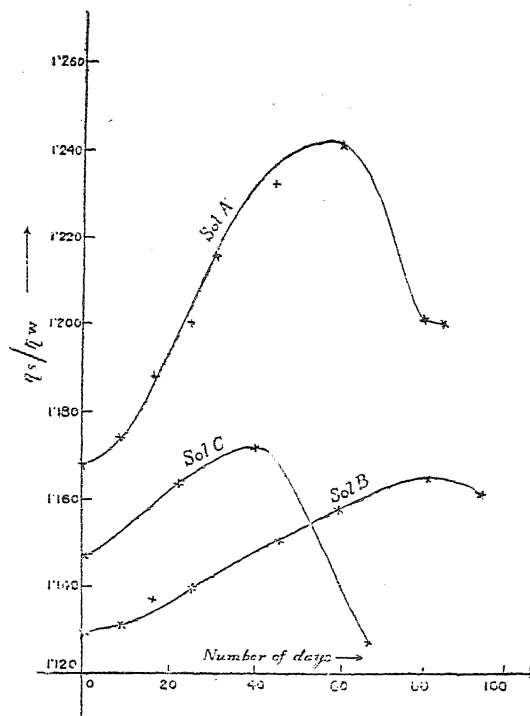
Time in days.	20 cms.	25 cms.	30 cms.
0	1.168	1.132	1.120
9	1.176	1.150	1.123
16	1.188	1.165	1.130
25	1.200	1.179	1.135
31	1.215	1.183	1.139
45	1.232	1.190	1.143
60	1.241	1.200	1.150
80	1.205	1.200	1.148
95	1.200	1.193	1.145

Table II.

Conc. of Sol B=19.85g/l of Solid  
matter.  
Conc. of Acetate ion=0.89 g/l

Time in days.	20 cms.	25 cms.	30 cms.
0	1.119	1.100	1.000
9	1.131	1.109	1.000
16	1.137	1.110	1.010
25	1.140	1.115	1.040
31	1.144	1.118	1.100
45	1.150	1.120	1.106
60	1.157	1.125	1.109
80	1.165	1.130	1.115
95	1.162	1.123	1.112

If we plot the values of  $\eta_s/\eta_w$  against time for the Sols A and B (say at 20 cms.), which shows the maximum changes on ageing we get the following curves :—



Although iron sols usually show great stability but after 80 days the sols were kept at a higher temperature to hasten their ageing. Moreover my earlier work on the effect of ageing on viscosity of sols has established certain important principles and the following table gives characteristic values of  $\eta_s/\eta_w$  in case of  $V_2O_5$  sol on ageing. The  $V_2O_5$  sol was prepared by the usual method of taking ammonium vanadate and treating it with conc. HCl, in a mortar and pestle and the red precipitate washed till it showed signs of peptization. The precipitate was treated with some quantity of water and kept for dialysis.

Conc. of Sol (c) = 9.828 gm. of  $V_2O_5$  per litre.

Table III

Time in days.	Sol C	Sol C/3	Sol C/9
0	1.147	1.049	1.020
5	1.155	1.036	1.007
22	1.163	1.047	1.020
47	1.170	1.048	1.020
65	1.127	1.041	1.013

In table III Sol C refers to the original sol, while sol C/3 and Sol C/9 refer to the original sol diluted three times and nine times respectively. It is clear from tables I, II and III that in the beginning there is a rise in the value of  $\eta_s/\eta_w$  and this rise continues for sometime, and after a certain period there is a fall in these values.

It has been reported earlier by me that in the case of pure sols the phenomena of ageing takes place quicker when compared with the impure sols. The process of dialysis helps the development of this loose structure.

#### DISCUSSION

The 'loose structure' can be summed up as a net result of two factors *viz.*, (i) the tendency of the particles to give rise to crystals and naturally developing some lattice-force between the particles and (ii) the tendency of the sol particles to decrease in stability on ageing, which results in the formation of larger aggregates, and bringing about a decrease in viscosity. The two factors have an opposite effect, first factor brings about an increase in the viscosity, whilst the second factor brings about a decrease. From the data obtained about the stability of sols particles towards electrolyte it appears that there is a constant fall in the amount of electrolyte required for coagulation, on ageing of the sol. This can be interpreted that the particles are always losing some amount of the adsorbed electrolyte, necessary for their stability and the charge on the particle continuously decreases, which decreases the force of repulsion between the different particles, a tendency favourable for the formation of larger aggregates. In the beginning the tendency of crystallization is much more rapid and as the curves show, it is clear that only after a certain period, the aggregation factor becomes very prominent, and overcomes easily the lattice-force developed in the system, and the fall in viscosity is recorded. The idea about the development of a lattice force is confirmed by the X-ray analysis of sols on ageing, and certain important conclusions drawn at an earlier stage *i.e.* (i) Purer the sol more easily the ageing takes place (ii) higher the conc. of the solid matter in the sol greater are the changes recorded in the viscosity of the system on ageing are further confirmed. The chances of a lattice formation are considerably increased in the case of pure and concentrated systems, hence the lattice-force developed in these systems is sufficiently large. Ageing in view of this is simply to provide the system sufficient rest and it is an important factor which favours crystallization. Hence my view is that the loose structure as predicted by Ghosh is a net effect of the lattice-force as a result of the tendency of the particles to crystallize, and the aggregation factor which results in decreasing the viscosity of the sol.

There is another important feature of this study of structural flow, under different shearing forces. It is evident that the values of  $\eta_s/\eta_w$  at higher pressure

are less than those at low pressures. In case of sols there are a number of factors which determine their stability, and naturally guide their structural flow. But if we apply this method in the case of solutions of electrolytes of suitable conc. and study  $\eta_{sp}/c$  at different shearing forces it can be helpful in calculating certain important Physical constants of the electrolytes.

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# THE DECOMPOSITION OF SODIUM MOLYBDATE BY HYDROCHLORIC ACID AND THE EFFECT OF AGEING ON THE SYSTEM.

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[Communicated by Dr. A. K. Dey.]

## ABSTRACT

There are different views regarding the extent of aggregations of Molybdenum in the system "Sodium Molybdate and Hydrochloric Acid" and the presence of octamolybdate in the solution. The authors have studied the decomposition of Sodium Molybdate by HCl with special reference to the effect of ageing on the system. Conductivity and PH measurements show that the aggregation of Molybdenum in this system proceeds till the formation of tetramolybdate and the aggregation is step-wise. Further, no evidence is found for the existence of octamolybdate. The effect of ageing on this system is definite though not predominant. It has been observed by us that the dimolybdate in the solution undergoes hydrolysis liberating molybdic acid on ageing. On ageing the solutions containing the trimolybdate undergo partial reduction which is indicated by the development of slight blue colour. Further, on ageing the tetramolybdate precipitate out in the form of a crystalline deposit.

The decomposition of Sodium Molybdate by HCl and the effect of ageing on the process has been studied conductometrically and by  $P_H$  measurements in these laboratories. The decomposition of the Sodium Molybdate by acids, both strong and weak, forming Polymolybdates received the attention of earlier workers. The decomposition products *i.e.* the Polymolybdates, the acid salts and sometimes the free molybdic acids of different compositions are of a complex nature. The solutions of molybdates like those of chromates, vanadates and tungstates, contain mixtures of different types in chemical equilibrium with one another and some times compounds other than those which were dissolved crystallise out. Attempts have been made to find out the constitution of the molybdates in some details but the views held by the various workers are contradictory. Jander and coworkers<sup>1</sup> showed from conductivity and diffusion measurements, that aggregation is possible giving Polymolybdates in the solutions containing 3, 6, 12 and 24 atoms of Mo. Britzinger<sup>2</sup> using electro-dialysis method, supported Jander's results. But Britton and German<sup>3</sup> from their electrometric studies observed that with the increase of  $H^+$  ion concentration on  $Na_2MoO_4$ , the aggregation of the acid part, or, more correctly,  $MoO_3$  goes on until a Polymolybdate  $Na_2 [O(MoO_3)_4]$  is formed in the solution and this salt decomposes by further increase of  $H^+$  ions, liberating the corresponding acid  $H_2 [O(MoO_3)_4]$  which ionises in solution to show increased conductivity. Again there are contradicting views as to the existence of Octamolybdate in the solution. Britton and German from the results of Walden<sup>4</sup>, Rosenheim<sup>5</sup>, and Rosenheim, Flex and Pinkser<sup>6</sup>

supported the presence of Octamolybdate in the solution. But Ghosh and Biswas<sup>7</sup> conclude from conductivity measurements that the octamolybdate supposed by Britton and German should be represented as a  $\text{NaH}[\text{O}(\text{MoO}_3)_4]$ , i.e., the acid salt of tetramolybdate. Mme. H. Frey<sup>8</sup> and H. Guiter<sup>9</sup> obtained Polymolybdates of different composition on crystallization of the solutions of P, ranging from 0.2 to 12.6, reference to which is made in this paper.

#### EXPERIMENTAL

In the following investigations, AR Sodium Molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) is used. The reagent HCl is of C. P. grade. The conductivity measurements are carried on "Doran New Conductivity Bridge". The PH measurements are made on the "Glass Electrode Beckman PH Meter".

A new electrical conductivity method for the study of the formation of Polymolybdate ion in solution, similar to a method suggested by Dey and Bhattacharya<sup>10</sup> for the study of the formation of complex ions in solutions has been adopted. The method consists in the determination of the electrical conductivities of the constituents separately and then that of the mixture. The physical properties of mixtures not yielding Polymolybdates are additive and hence any difference between the sum of the conductivities of the constituents and the observed conductivity of the mixture suggests complex formation. If the percentage difference in the conductivities of the mixtures of different compositions be found and plotted in a graph against the composition of the mixture, the formation of polymolybdates can be interpreted from the curve. The  $\text{P}_\text{H}$  of the HCl solution and that of Sodium Molybdate is measured individually and then that of the mixture. Any increase in the  $\text{P}_\text{H}$  of the mixture indicates the utilization of HCl for the formation of a polymolybdate in the solution.

#### DISCUSSION

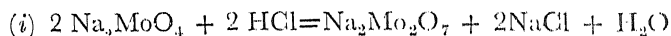
The conductivity results of mixtures of fresh and aged solutions are summarized in Table I. The  $\text{P}_\text{H}$  values of these mixtures are given in Table II. Figure I shows the graph of percentage difference in conductivity plotted against the composition. The dotted curve is that of aged mixtures. Figure II shows the graph of  $\text{P}_\text{H}$  values plotted against the composition, and here too the dotted curve is that of aged mixtures.

The mixtures of Sodium Molybdate and HCl from ratio 1 : 0.25 to 1 : 4 are studied. The results show that there is a very considerable percentage fall in conductivity even with the mixture containing the least concentration of HCl. The maximum percentage difference in conductivity is observed with the mixture of composition 1 : 2 after which it gradually decreases as we reach the mixture of composition 1 : 4. The fall of conductivity in all these mixtures is evidently due to the formation of Polymolybdates by the decomposition of Sodium Molybdate by



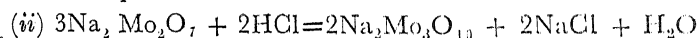
HCl. That HCl is utilised in all these sets is indicated by the increase of  $P_H$  in the solutions after the addition of Sodium Molybdate (Table II).

The  $P_H$  of the mixtures 1–6 does not vary much but the composition varies, *i.e.*, from 1 : 0.25 to 1 : 1. The percentage fall in conductivity shows a gradual increase in these mixtures. Hence it can be concluded that all the HCl in these mixtures, Nos. 1 to 6, is utilized but not all the Sodium Molybdate to form a Polymolybdate since at least one molecule of HCl is required for every molecule of Sodium Molybdate to give the dimolybdate. The decomposition of Sodium Molybdate till the ratio of the mixture reaches 1 : 1 can be represented by the equation:



In mixtures of compositions of ratio less than 1 : 1, Sodium Molybdate also exists in addition to the products  $\text{Na}_2\text{Mo}_2\text{O}_7$  and NaCl since sufficient HCl is not present to decompose all the Sodium Molybdate. Therefore the conductivity of the mixtures, till the composition reaches the ratio 1 : 1, is due to  $\text{Na}_2\text{MoO}_4$ ,  $\text{Na}_2\text{Mo}_2\text{O}_7$  and NaCl which give ions of less mobility than the ions of the reactants. That dimolybdate exists in these mixtures, 1–6, is supported by the fact that Mme H. Frey and H. Guiter (*loc. cit.*) obtained this salt on crystallisation from solutions of  $P_H$  5.65 which is really in agreement with the  $P_H$  values of the above mixtures. The conversion of Sodium Molybdate to Sodium Dimolybdate is complete at the mixture of composition 1 : 1, as is seen in equation (i) where only one molecule of HCl is required for every molecule of  $\text{Na}_2\text{MoO}_4$ .

At composition 1 : 1.28, the  $P_H$  value of the mixture falls (Table II, Figure II) and the percentage difference in conductivity increases further (Table I, Figure I). This change is steady till the composition comes to 1 : 1.6. Therefore the transformation of dimolybdate into trimolybdate starts after the composition exceeds the ratio 1 : 1 and is complete at the ratio 1 : 1.6. The conversion of dimolybdate into trimolybdate is represented as



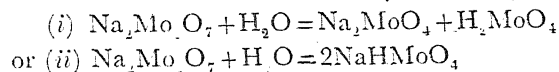
It is clear from the equation (ii) that every molecule of Sodium dimolybdate requires  $2/3$  or 0.66 molecules of HCl to be converted into the next higher polymolybdate, *i.e.*, the trimolybdate; if we start from Sodium molybdate, every molecule of it requires 1.66 molecules of HCl to form the trimolybdate—which is in accordance with the observed results. H. Guiter (*loc. cit.*) also reported that the trimolybdate crystallises with 1.5  $\text{H}_2\text{O}$  from solutions of  $P_H$  4.5, which also is in accordance with our results (Table II).

When the composition exceeds 1 : 1.6, the formation of tetramolybdate starts from the trimolybdate and is complete when the composition reaches 1 : 2. At this point, the percentage fall in conductivity is maximum and the  $P_H$  falls considerably due to the stable tetramolybdate in the solution.

By further increase of HCl concentration to give mixtures of composition 1 : 2 to 1 : 4, it is observed that the percentage fall of conductivity decreases gradually and the  $P_H$  falls very considerably from that of the previous mixtures. (Table II). This change might be due to the decomposition of Sodium tetramolybdate to give a polymolybdic acid which gives ions of greater mobility and decreases the  $P_H$  of the solution as pointed out by Britton and German (loc. cit) or due to the formation of the acid tetramolybdate ( $\text{NaHMo}_4\text{O}_{10}$ ) as shown by Ghosh and Biswas. (loc. cit.)

It may be further pointed out that, contrary to the conclusions of Britton and German, there is no evidence of the formation of Sodium octamolybdate or any higher polymolybdate of sodium in solution, since the percentage fall in conductivity decreases instead of increasing, after the formation of sodium tetramolybdate.

*The Effect of Ageing:* The mixtures containing the polymolybdates which have been so far discussed are allowed to age for 3 months. The results are given in Tables I and II, and the graphs are plotted similar to those of fresh mixtures. (The curves for the aged mixtures are drawn in dotted lines). The curves of both conductivity and  $P_H$  measurements (shown in Figures I and II in dotted lines) show deviation from the curves for fresh mixtures till the composition reaches 1 : 1. After the composition exceeds 1 : 1, the curves of both conductivity and  $P_H$  travel almost with those of fresh mixtures even after ageing. The decrease in percentage difference in conductivity and the fall in  $P_H$  in mixtures before the composition 1 : 1 is reached, is due to the formation of a different product in solution which provides ions of a greater mobility—evidently H ions. This is possibly due to the hydrolysis of  $\text{Na}_2\text{Mo}_2\text{O}_7$  formed in fresh solutions in two ways:—



The liberation of molybdic acid is more probable than that of the acid molybdate  $\text{NaHMoO}_4$ , the existence of which is doubtful.

The absence of change either in the conductivity of  $P_H$  after the composition exceeds 1 : 1 shows that the polymolybdates formed in fresh solutions are quite stable even after considerable ageing.

A good deal of change in physical properties is observed between fresh and aged mixtures. (The results are described in Table I).

An yellowish-green to blue colour is developed on ageing in mixtures 7—9 in which the formation of the trimolybdate is described above. The development of colour on ageing is possibly due to partial reduction. In mixtures 10—12, a white crystalline deposit is formed on ageing which is the tetramolybdate itself.

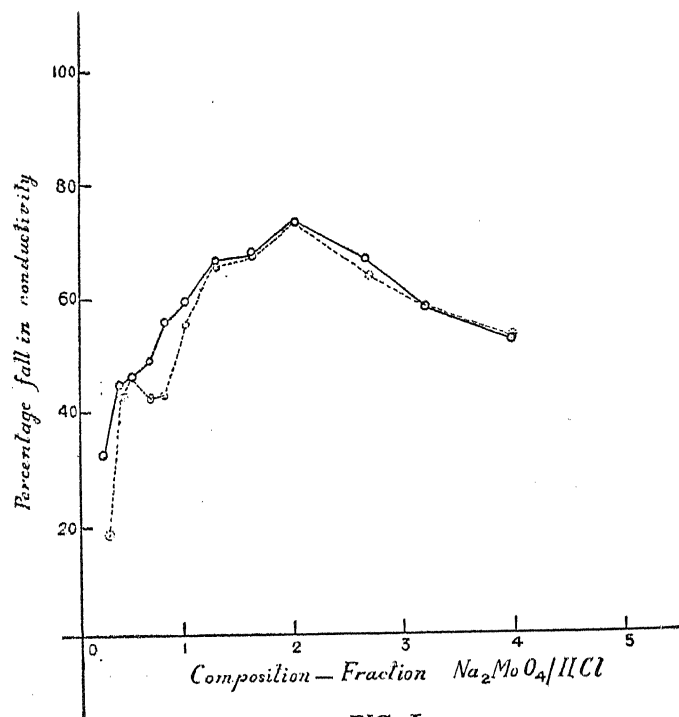


FIG I

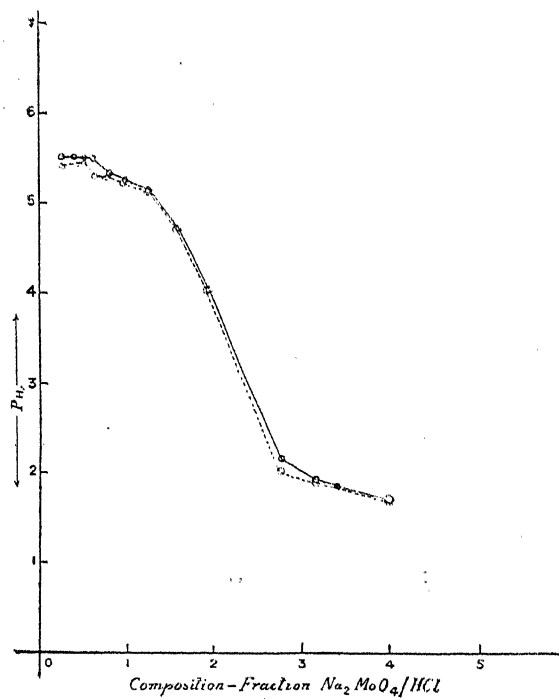


FIG II

Table I.  
(Temperature 30°C)  
(Conductivity of  $M/32 \text{ Na}_2\text{MoO}_4$  Sol. =  $66.78 \times 10^{-4}$  mhos)

No.	Conc. HCl sol.	Conc. $\text{Na}_2\text{MoO}_4$ sol.	Ratio of $\text{Na}_2\text{MoO}_4$ : HCl.	Conductivity of HCl sol. $10^{-4}$ mhos.	Sum of the conduc- tivities of the con- stituents $10^{-4}$ mhos.	Observed conducti- vity of the mix- ture $10^{-4}$ mhos.	Percentage fall in conductivity.	Observed conducti- vity of the mix- ture after ageing $10^{-4}$ mhos.	Percentage fall in conductivity after ageing.	Physical appearance.	
										Before ageing.	After ageing.
1	M/128	M/32	1 : 0.25	25.19	91.97	64.12	30.27	54.88	18.58	Colourless solution.	Colourless solution.
2	M/80	"	1 : 0.4	49.62	116.40	64.2	44.92	66.79	42.62	"	"
3	M/64	"	1 : 0.5	57.25	124.03	66.04	46.77	66.79	46.13	"	"
4	M/50	"	1 : 0.64	62.98	129.76	64.51	49.79	74.42	42.76	"	"
5	M/40	"	1 : 0.8	82.06	148.84	65.64	55.85	85.88	62.27	"	"
6	M/32	"	1 : 1	99.24	166.02	66.79	59.70	74.42	65.21	"	"
7	M/25	"	1 : 1.28	133.60	200.38	66.79	66.68	68.71	65.77	"	Greenish yellow to blue.
8	M/20	"	1 : 1.6	156.50	223.28	68.71	67.50	70.64	68.27	"	"
9	M/16	"	1 : 2	190.80	257.58	70.62	72.56	73.67	71.41	"	"
10	M/12.5	"	1 : 2.8	271.00	337.78	112.60	66.68	120.20	64.63	"	White crystal- line deposit.
11	M/10	"	1 : 3.2	297.70	364.78	152.70	58.10	150.80	58.51	"	"
12	M/8	"	1 : 4	374.00	440.78	209.90	52.37	206.10	53.21	"	"

*Table II.*  
(Temperature 30°C)

Set No.	Ratio $\text{Na}_2\text{MoO}_4 : \text{HCl}$ .	$\text{P}_\text{H}$ of HCl solution alone	$\text{P}_\text{H}$ of $\text{Na}_2\text{MoO}_4$ solution alone	$\text{P}_\text{H}$ of the mixture of $\text{Na}_2\text{MoO}_4$ and HCl to give ratio in Column 2.	$\text{P}_\text{H}$ of the Mixture after ageing.
1	1 : 0.25	2.4	6.8	5.5	5.4
2	1 : 0.4	2.3	6.8	5.5	5.4
3	1 : 0.5	2.2	6.8	5.5	5.5
4	1 : 0.64	2.1	6.8	5.5	5.3
5	1 : 0.8	2.0	6.8	5.35	5.31
6	1 : 1	1.9	6.8	5.25	5.20
7	1 : 2.28	1.8	6.8	5.15	5.15
8	1 : 1.6	1.7	6.8	4.7	4.65
9	1 : 2	1.65	6.8	4.0	4.0
10	1 : 2.8	1.5	6.8	2.15	2.0
11	1 : 3.2	1.45	6.8	1.9	1.9
12	1 : 4	1.4	6.8	1.7	1.7

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# STUDIES IN THE AMPHOTERIC NATURE OF HYDRATED CHROMIUM OXIDE AND THE DETERMINATION OF ITS ISOELECTRIC POINT

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Hydrous chromic oxide, freshly precipitated from a chromic salt solution with an alkali or ammonia is readily soluble in acids giving the corresponding salts, and is peptized by alkali hydroxides with the formation of a negative sol which suggest its amphoteric nature. On standing the oxide undergoes ageing phenomenon thus causing a change in physical character accompanied by a marked decrease in solubility and reactivity. The adsorptive capacity of the hydrous chromic oxide samples A, B and C precipitated with 10% excess, equivalent and 10% deficient alkali has already been reported by us (1) in one of the communications in which adsorption of both basic and acidic dyestuffs has been recorded. The difference in adsorptive capacity of the samples clearly show their different chemical reactivity. It has been shown (2) that the nature of the hydrous oxide samples depends on the amount of alkali used for precipitation. The use of hydrated chromium oxide as a mordanting agent is well known. Blitz (3) studied the adsoption of alizarin by chromium hydroxide. Dey and Ghosh (4) have shown that the adsorption of the anion or the cation by hydrated oxide, is related to the hydrogen-ion concentration of the medium. It is well recognised in the cases of such amphoteric bodies like proteins, that the adsorption of a cation or an anion depends on the hydrogen-ion concentration of the medium in which the protein is suspended. Thus Loeb (5) has shown that a protein like gelatin takes up silver ions from silver nitrate solution, when the pH value of the solution is greater than 4.7, and it takes up ferrocyanide ions, when the pH is less than this value, which is that for the isoelectric point of gelatin.

In this paper hydrous oxide of chromium has been precipitated from its salt solutions by using different amounts of an alkali like sodium hydroxide and three samples A, B and C have been obtained as given in the table below.

*Table A.*

Temperature 25°C.			
100 ml of M/3 CrCl <sub>3</sub> solution = 32.5 ml of 2.15 M NaOH solution.			
Sample.	Volume of CrCl <sub>3</sub>	Volume of NaOH.	Remarks.
A	100 ml	35.75 ml.	10% excess alkali
B	„	32.50 ml	Equivalent alkali.
C	„	29.25 ml.	10 % deficient alkali

The hydrated oxide samples thus obtained, were washed with water till free from chromium, hydroxyl ions and chloride ions. The precipitates were made into suspensions and the chromium content was estimated. The volume was adjusted to make the amount of chromium constant in each suspension. The object of this investigation was to study the amphoteric nature of the hydrated oxide, as related to the adsorption of a cation or of an anion from an added dye solution. We have already shown (6), that substances of basic character adsorb hydrogen ions and anions, while those of acid character have a remarkable preferential adsorption for hydroxyl ions and cations.

#### EXPERIMENTAL.

The hydrous oxide samples as obtained above contained 8.28 gms. per litre  $\text{Cr}_2\text{O}_3$  in the suspension. To 2 ml of the homogeneous suspension were added different volumes of M/100 sodium hydroxide or sulphuric acid solution, measured from a microburette. The dyes used were respectively 0.1% solutions of methylene blue, malachite green, orange II and congo red. To the precipitates suspended in media of different hydrogen ion concentrations, were added 2 ml of the dye solutions, total volume kept 10 ml, and the precipitate filtered the next day. The washing was done till the filtrates were free from the dyes, and the colour of the precipitates examined. The observations are recorded in tables I to XII.

Table I.

Adsorption of methylene-blue. Sample A.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.	Examination of the colour of the		
	precipitate.	supernatant liquid.	
2.0 × 10 <sup>-4</sup> M. NaOH	Deep blue	Faint blue.	
1.5        "	"	"	
1.0        "	"	"	
0.5        "	"	"	
Neutral	"	"	
0.5 × 10 <sup>-4</sup> M. H <sub>2</sub> SO <sub>4</sub>	"	"	
1.0        "	Light blue	"	
1.5        "	"	"	
2.5        "	Green	Deep blue.	
3.0        "	"	"	

Table II.

Adsorption of methylene blue.  
Sample B.

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Deep blue	Faint blue.
2.0        "	"	"
1.5        "	"	"
1.0        "	Light blue	"
0.5        "	Deep green	Deep blue.
Neutral	"	"
$0.5 \times 10^{-4}$ M. $H_2SO_4$	"	"
1.0        "	"	"
1.5        "	"	"
2.0        "	"	"
2.5        "	"	"

Table III.

Adsorption of methylene-blue.  
Sample C.

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$4.5 \times 10^{-4}$ M. NaOH	Deep blue	Faint blue.
4.0        "	Light blue	"
3.5        "	Deep green	Deep blue.
3.0        "	"	"
1.5        "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. $H_2SO_4$	"	"
1.0        "	"	"
1.5        "	"	"
2.0        "	"	"
2.5        "	"	"



Table IV.

Adsorption of malachite-green.  
Sample A.

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
2.0 × 10 <sup>-3</sup> M. NaOH	Light blue	Colourless.
1.5        "        "	"	"
1.0        "        "	"	"
0.5        "        "	"	"
Neutral	"	"
0.5 × 10 <sup>-3</sup> M. H <sub>2</sub> SO <sub>4</sub>	"	"
1.0        "        "	"	"
1.5        "        "	"	"
2.0        "        "	"	"
2.5        "        "	Deep Green	Deep bluish-green.
3.0        "        "	"	"

Table V.

Adsorption of malachite-green.  
Sample B.

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
2.5 × 10 <sup>-3</sup> M. NaOH	Light blue	Colourless.
2.0        "        "	"	"
1.5        "        "	"	"
1.0        "        "	"	"
0.5        "        "	Deep green	Deep-bluish green.
Neutral	"	"
0.5 × 10 <sup>-4</sup> M. H <sub>2</sub> SO <sub>4</sub>	"	"
1.0        "        "	"	"
1.5        "        "	"	"
2.0        "        "	"	"
2.5        "        "	"	"

Table VI.

Adsorption of malachite-green.  
Sample B.

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$4.5 \times 10^{-4}$ M. NaOH	Light blue	Colourless.
4.0        "	"	"
3.5        "	Deep Green	Deep bluish-green.
3.0        "	"	"
1.5        "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. $\text{H}_2\text{SO}_4$	"	"
1.0        "	"	"
1.5        "	"	"
2.0        "	"	"
2.5        "	"	"

Table VII.

Adsorption of Orange II.  
Sample A.

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$0.2 \times 10^{-4}$ M. NaOH	Deep Green	Deep Yellow.
1.5        "	"	"
1.0        "	"	"
0.5        "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. $\text{H}_2\text{SO}_4$	"	"
1.0        "	"	"
1.5        "	"	Light yellow.
2.0        "	"	"
2.5        "	Light Yellow	Colourless.
3.0        "	Deep Yellow	Colourless.

Table VIII.

Adsorption of Orange II. Sample B.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.		Examination of the colour of the	
		precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH		Deep Green	Deep yellow.
2.0	"	"	"
1.5	"	"	"
1.0	"	"	"
0.5	"	Yellowish green	Light yellow.
Neutral		Deep yellow	Colourless.
$0.5 \times 10^{-4}$ M. $H_2SO_4$		"	"
1.0	"	"	"
1.5	"	"	"
2.0	"	"	"
2.5	"	"	"

Table IX.

Adsorption of Orange II. Sample C.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.		Examination of the colour of the	
		precipitate.	supernatant liquid.
$4.5 \times 10^{-4}$ M. NaOH		Deep green	Deep yellow.
4.0	"	"	"
3.5	"	Yellowish green	Light yellow.
3.0	"	Deep yellow	Colourless.
1.5	"	"	"
Neutral		"	"
$0.5 \times 10^{-4}$ M. $H_2SO_4$		"	"
1.0	"	"	"
1.5	"	"	"
2.0	"	"	"
2.5	"	"	"

Table X.

Adsorption of Congo-red.  
Sample A.

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.0 \times 10^{-4}$ M. NaOH	Deep green	Deep green.
1.5     "	"	"
1.0     "	"	"
0.5     "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. $H_2SO_4$	"	"
1.0     "	"	"
1.5     "	"	"
2.0     "	"	"
2.5     "	Reddish green	Light red.
3.0     "	Deepred	Colourless.

Table XI.

Adsorption of Congo-red.  
Sample B.

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Deep green	Deep green.
2.0     "	"	"
1.5     "	"	"
1.0     "	"	"
0.5     "	Reddish green	Light red.
Neutral	Deep red	Colourless.
$0.5 \times 10^{-4}$ M. $H_2SO_4$	"	"
1.0     "	"	"
1.5     "	"	"
2.0     "	"	"
2.5     "	"	"

Table XII.

Adsorption of Congo-red. Sample C.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.	Examination of the colour of the		
	precipitate.	supernatant liquid.	
4.50 × 10 <sup>-4</sup> M. NaOH	Deep green	Deep red.	
4.0        "        "	"	"	
3.5        "        "	Reddish green	Light red.	
3.0        "        "	Deep red	Colourless.	
1.5        "        "	"	"	
Neutral        "	"	"	
0.5 × 10 <sup>-4</sup> M. H <sub>2</sub> SO <sub>4</sub>	"	"	
1.0        "        "	"	"	
1.5        "        "	"	"	
2.0        "        "	"	"	
2.5        "        "	"	"	

The samples of the hydrous oxide were kept in jena glass bottles for a period of 4 months. Tables XIII, XIV and XV record the adsorption of Congo-red by the aged samples.

Table XIII.

Adsorption of Congo-red Sample A.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.	Examination of the colour of the		
	precipitate.	supernatant liquid.	
2.0 × 10 <sup>-4</sup> M. NaOH	Deep green	Deep red.	
1.5        „	„	„	
1.0        „	„	„	
0.5        „	„	„	
Neutral	„	„	
0.5 × 10 <sup>-4</sup> M. H <sub>2</sub> SO <sub>4</sub>	„	„	
1.0        „	„	„	
1.5        „	„	„	
2.0        „	Reddish green	Light red.	
2.5        „	Deep red	Colourless.	
3.0        „	„	„	

Table XIV.

Adsorption of Congo-red. Sample B.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.		Examination of the colour of the	
		precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH		Deep green	Deep red.
2.0	"	"	"
1.5	"	"	"
1.0	"	Reddish green	Light red.
0.5	"	Deep red.	Colourless.
Neutral		"	"
$0.5 \times 10^{-4}$ M. $H_2SO_4$		"	"
1.0	"	"	"
1.5	"	"	"
2.0	"	"	"
2.5	"	"	"

Table XV

Adsorption of Congo-red. Sample C.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.		Examination of the colour of the	
		precipitate.	supernatant liquid.
$5.0 \times 10^{-4}$ M. NaOH		Deep green	Deep red.
4.5	"	"	"
4.0	"	Reddish green	Light red.
3.5	"	Deep red	Colourless.
3.0	"	"	"
Neutral		"	"
$1.0 \times 10^{-4}$ M. $H_2SO_4$		"	"
1.5	"	"	"
2.0	"	"	"
2.5	"	"	"

The three samples A, B and C of the hydrous oxide were heated and the adsorption of the dye congo-red has been recorded in tables XVI to XVIII.

Table XVI.

Adsorption of Congo-red. Sample A.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.	Examination of the colour of the		
	precipitate.	supernatant liquid.	
2.0 × 10 <sup>-4</sup> M. NaOH	Deep green	Deep red.	
1.5        "	"	"	
1.0        "	"	"	
0.5        "	"	"	
Neutral	"	"	
0.5 × 10 <sup>-4</sup> M. H <sub>2</sub> SO <sub>4</sub>	"	"	
1.0        "	"	"	
1.5        "	Reddish green	Light red.	
2.0        "	Deep red	Colourless.	
2.5        "	"	"	
3.0        "	"	"	

Table XVII.

Adsorption of Congo-red. Sample B.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.	Examination of the colour of the		
	precipitate.	supernatant liquid.	
3.0 × 10 <sup>-4</sup> M. NaOH	Deep green	Deep red.	
2.5        "	"	"	
2.0        "	Reddish Green	Light red.	
1.5        "	Deep red	Colourless.	
1.0        "	"	"	
0.5        "	"	"	
Neutral	"	"	
1.0 × 10 <sup>-4</sup> M. H <sub>2</sub> SO <sub>4</sub>	"	"	
1.5        "	"	"	
2.0        "	"	"	
2.5        "	"	"	

Table XVIII.

Adsorption of Congo-red. Sample C.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.		Examination of the colour of the	
		precipitate.	supernatant liquid.
$6.0 \times 10^{-4}$ M. NaOH		Deep green	Deep red.
5.5	"	"	"
5.0	"	"	"
4.5	"	Reddish Green	Light red.
4.0	"	Deep red	Colourless.
3.5	"	"	"
3.0	"	"	"
Neutral	"	"	"
$1.0 \times 10^{-4}$ M. $H_2SO_4$		"	"
1.5	"	"	"
2.0	"	"	"
2.5	"	"	"

Incidentally it was thought worthwhile to determine the iso-electric points of different samples of the hydrous oxides. The pH of the iso-electric samples were determined by the electrometric method. The values obtained are given in the table below.

Table XIX.

Iso-electric point of hydrated chromium oxide. Temperature 25°C.			
Sample	Ordinary temperature pH.	Slow ageing for 4 months pH.	Rapid ageing by heating pH.
A	6.49	6.62	6.76
B	6.68	6.96	7.18
C	7.10	7.29	7.40

It is found that the hydroxide sample C behaves as iso-electric in the alkaline region whereas the other samples have their iso-electric points in the acidic region. It is observed that in all the cases these iso-electric points shift towards the alkaline region on ageing.



The above table clearly shows, that the hydrated chromium oxide samples A, B and C behave differently in their character. The sample A is capable of adsorbing the anions of the acid dyes only when the medium is slightly acidic whilst the sample C is capable to do so even in the neutral medium pH 7. The sample B lies intermediate between the samples A and C. It should be recalled that the sample A has more acidic property which is to be suppressed in slightly acidic medium before it is capable of adsorbing the anion of a dye-stuffs. The sample A, precipitated with excess alkali has been found to possess a good adsorptive capacity for the cations. Sample C as we have already shown (2) possesses a good adsorptive capacity for the anions because of its predominantly basic character and it is found to be associated with fair amount of  $\text{Cl}^-$  ions during the course of its preparation.

It should be also noted that with ageing carried out either by keeping the hydrated oxide in water or by warming it, the iso-electric point show a variation in all the cases and that it shifts towards the alkaline region. This indicates the variations in the nature of the solid surface with age and it is interesting to conclude that the acidic character of chromium hydroxide quickly decreases than its basic property. This is in line with our observations already made with the different samples that the ageing is more rapid for the sample A which has more acidic behaviour.

Further work on hydrous oxides is in progress in this laboratory which will form the subject matter of subsequent communications:

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# STUDIES IN THE AMPHOTERIC NATURE OF HYDRATED ALUMINIUM OXIDE AND THE DETERMINATION OF ITS ISOELECTRIC POINT

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The gelatinous oxide freshly precipitated in the cold dissolves in acids and alkalis forming salts, and is readily peptized by certain dilute acids and salts, which shows its amphoteric nature. The hydrous oxide on ageing undergoes a change in its adsorptive property accompanied by a marked decrease in solubility towards acids and alkalis. We have reported in several communications (1) that the nature of the hydrous oxide samples depends on the amount of alkali used for precipitation. The adsorption of the anion or the cation by the hydrated oxide is related to the hydrogen ion concentration of the medium has been shown by Dey and Ghosh (2). The use of alumina as a mordanting agent is well known. For a long time lakes were believed to be definite chemical compounds between the dye and the oxide. This belief was largely based on the observation that acid dyes in which the anion is the coloured radical are taken up to a great extent only by basic mordants and basic dyes only by acid mordants. Thus alumina takes up the acid dye alizarin under suitable conditions, and it was assumed that a definite aluminium alizarate was formed.

It is well recognised in the cases of such amphoteric bodies like proteins, that the adsorption of a cation or an anion depends on the hydrogen ion concentration of the medium in which the protein is suspended. Thus Loeb (3) has shown that gelatin takes up silver or ferrocyanide ions from their respective salt solutions when the pH value of the medium is either greater or less than 4.7 respectively.

## EXPERIMENTAL.

The samples A, B and C of hydrated oxide of aluminium were obtained by using excess, equivalent and deficient amounts of alkali for the precipitation. The samples thus obtained were washed with water to free them from electrolytes, made into a suspension and amount of aluminium was estimated. The volume of the suspension was adjusted to make the amount of aluminium constant in each of the suspension.

The amount of  $\text{Al}_2\text{O}_3$  in each suspension was 4.44 gms. per litre.

To 2 ml of the homogeneous suspension were added different volumes of M/100 sodium hydroxide or sulphuric acid solution, measured from a microburette. The dyes used were 0.1% solutions of fuchsin (basic), methylene blue, malachite green and fuchsin (acid). To the precipitates suspended in media of different hydrogen-ion concentrations, were added 2 ml of the dye solutions, total volume kept

10 ml, and the precipitates filtered the next day. The washing was done till the filtrates were free from the dyes, and the colour of the precipitates examined. The observations are recorded in Tables I to XII.

Table I.

Adsorption of Fuchsin (Basic).

Temperature 25°.

Sample A.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Deep red	Colourless.
2.0        "	"	"
1.5        "	"	"
1.0        "	"	"
0.5        "	"	"
Neutral	"	"
$0.5 \times 10^{-1}$ M. $H_2SO_4$	"	"
1.0        "	"	"
1.5        "	Light red	Light red.
2.0        "	"	"
2.5        "	"	"

Table II.

Adsorption of Fuchsin (Basic).

Temperature 25°.

Sample B.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Deep red	Colourless.
2.0        "	"	"
1.5        "	"	"
1.0        "	"	"
0.5        "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. $H_2SG_4$	Light red	Light red.
1.0        "	"	"
1.5        "	"	"
2.0        "	"	"
2.5        "	"	"

Table III.

Adsorption of Fuchsin (Basic).		Temperature 25°.	
Sample C.			
Final concentration of acid or alkali in the mixture.	Examination of the colour of the		
	precipitate.	supernatant liquid.	
2.5 × 10 <sup>-4</sup> M. NaOH	Deep red	Colourless.	
2.0        "        "	"	"	
1.5        "        "	"	"	
1.0        "        "	"	"	
0.5        "        "	Light red	Light red.	
Neutral	"	"	
0.5 × 10 <sup>-4</sup> M. H <sub>2</sub> SO <sub>4</sub>	"	"	
1.0        "        "	"	"	
1.5        "        "	"	"	
2.0        "        "	"	"	
2.5        "        "	"	"	

Table IV.

Adsorption of methylene blue.		Temperature 25°.	
Sample A.			
Final concentration of acid or alkali in the mixture.	Examination of the colour of the		
	precipitate.	supernatant liquid.	
2.5 × 10 <sup>-1</sup> M. NaOH	Deep blue	Light blue.	
2.0        „	„	„	
1.5        „	„	„	
1.0        „	„	„	
0.5        „	„	„	
Neutral	„	„	
0.5 × 10 <sup>-4</sup> M. H <sub>2</sub> SO <sub>4</sub>	„	„	
1.0        „	„	„	
1.5        „	Light blue	Deep blue.	
2.0        „	„	„	
2.5        „	„	„	

Table V.

Adsorption of methylene blue.

Temperature 25°.

Sample B.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-1}$ M. NaOH	Deep blue	Light blue.
2.0     "	"	"
1.5     "	"	"
1.0     "	"	"
0.5     "	"	"
Neutral	Light blue	Deep blue.
$0.5 \times 10^{-1}$ M. $H_2SO_4$	Colourless.	"
1.0     "	"	"
1.5     "	"	"
2.0     "	"	"
2.5     "	"	"

Table VI.

Adsorption of methylene blue.

Temperature 25°.

Sample C.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-1}$ M. NaOH	Deep blue	Light blue.
2.0     "	"	"
1.5     "	"	"
1.0     "	Light blue.	"
0.5     "	Colourless.	Deep blue.
Neutral	"	"
$0.5 \times 10^{-1}$ M. $H_2SO_4$	"	"
1.0     "	"	"
1.5     "	"	"
2.0     "	"	"
2.5     "	"	"

Table VII.

Adsorption of malachite green.  
Sample A.

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Deep blue	Colourless.
2.0        "	"	"
1.5        "	"	"
1.0        "	"	"
0.5        "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. H <sub>2</sub> SO	"	"
1.0        "	"	"
1.5        "	Light blue	Deep blue.
2.0        "	"	"
2.5        "	"	"

Table VIII.

Adsorption of malachite green.  
Sample B.

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Deep blue	Colourless.
2.0        "	"	"
1.5        "	"	"
1.0        "	"	"
0.5        "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. H <sub>2</sub> SO <sub>4</sub>	Light blue	Deep blue.
1.0        "	"	"
1.5        "	"	"
2.0        "	"	"
2.5        "	"	"

Table IX.

Adsorption of malachite green.

Temperature 25°.

Sample C.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-1}$ M. NaOH	Deep blue	Colourless.
2.0        "	"	"
1.5        "	"	"
1.0        "	"	"
0.5        "	Light blue	Deep blue.
Neutral	"	"
$0.5 \times 10^{-4}$ M. $H_2SO_4$	"	"
1.0        "	"	"
1.5        "	"	"
2.0        "	"	"
2.5        "	"	"

Table X.

Adsorption of Fuchsin (acidic).

Temperature 25°.

Sample A.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Colourless	Deep red.
2.0        "	"	"
1.5        "	"	"
1.0        "	"	"
0.5        "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. $H_2SO_4$	"	"
1.0        "	"	"
1.5        "	Light red	Light red.
2.0        "	"	"
2.5        "	Deep red	Colourless.

Table XI.

Adsorption of Fuchsin (acidic).

Temperature 25°.

Sample B.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Colourless	Deep red.
2.0        "	"	"
1.5        "	"	"
1.0        "	"	"
0.5        "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. $H_2SO_4$	Light red	Light red.
1.0        "	"	"
1.5        "	"	"
2.0        "	Deep red	Colourless.
2.5        "	"	"

Table XII.

Adsorption of Fuchsin (Acidic).

Temperature 25°.

Sample G.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Colourless	Deep red.
2.0        "	"	"
1.5        "	"	"
1.0        "	"	"
0.5        "	Light red	Light red.
Neutral	"	"
$0.5 \times 10^{-4}$ M. $H_2SO_4$	"	"
1.0        "	Deep red	Colourless.
1.5        "	"	"
2.0        "	"	"
2.5        "	"	"

The following tables XIII, XIV and XV record the adsorption of the dye malachite green by the hydrated oxide samples aged for 4 months period.



Table XIII.

Adsorption of malachite green.

Temperature 25°.

Sample A.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Deep blue	Colourless.
2.0     "	"	"
1.5     "	"	"
1.0     "	"	"
0.5     "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. $H_2SO_4$	"	"
1.0     "	Light blue	Deep blue.
1.5     "	"	"
2.0     "	"	"
2.5     "	"	"

Table XIV.

Adsorption of malachite green.

Temperature 25°.

Sample B.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Deep blue	Colourless.
2.0     "	"	"
1.5     "	"	"
1.0     "	"	"
0.5     "	"	"
Neutral	Light blue	Deep blue.
$0.5 \times 10^{-4}$ M. $H_2SO_4$	"	"
1.0     "	"	"
2.0     "	"	"
2.5     "	"	"

Table XV.

Adsorption of malachite green  
Sample C.

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Deep blue	Colourless.
2.0     "	"	"
1.5     "	"	"
1.0     "	"	"
0.7     "	Light blue.	Deep blue.
0.5     "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. H <sub>2</sub> SO <sub>4</sub>	"	"
1.0     "	"	"
1.5     "	"	"
2.0     "	"	"
2.5     "	"	"

The following tables XVI, XVII and XVIII record the adsorption of the dye malachite green by the hydrated oxide samples aged by heating.

Table XVI.

Adsorption of malachite green.  
Sample A

Temperature 25°.

Final concentration of acid or alkali in the mixture.	Examination of the colour of the	
	precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH	Deep green	Colourless.
2.0     "	"	"
1.5     "	"	"
1.0     "	"	"
0.5     "	"	"
Neutral	"	"
$0.5 \times 10^{-4}$ M. H <sub>2</sub> SO <sub>4</sub>	Light blue	Deep blue.
1.0     "	"	"
1.5     "	"	"
2.0     "	"	"
2.5     "	"	"

Table XVII.

Adsorption of malachite green. Sample B.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.		Examination of the colour of the	
		precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH		Deep blue	Colourless.
2.0	"	"	"
1.5	"	"	"
1.0	"	"	"
0.5	"	Light blue	Deep blue.
Neutral		"	"
$0.5 \times 10^{-4}$ H <sub>2</sub> SO <sub>4</sub>		"	"
1.0	"	"	"
1.5	"	"	"
2.0	"	"	"
2.5	"	"	"

Table XVIII.

Adsorption of malachite green. Sample C.		Temperature 25°.	
Final concentration of acid or alkali in the mixture.		Examination of the colour of the	
		precipitate.	supernatant liquid.
$2.5 \times 10^{-4}$ M. NaOH		Deep blue	Colourless.
2.0	"	"	"
1.5	"	"	"
1.0	"	"	"
0.5	"	Light blue	Deep blue.
Neutral		"	"
$0.5 \times 10^{-4}$ M. H <sub>2</sub> SO <sub>4</sub>		"	"
1.0	"	"	"
1.5	"	"	"
2.0	"	"	"
2.5	"	"	"

It was thought worth while to determine the iso-electric points of different samples of the hydrated oxides. The pH of the isoelectric samples were determined by the electrometric method. The values obtained are given in table below :—

Table XIX.

Sample.	Iso-electric point of hydrated aluminium oxide. Temperature 25°C.		
	Ordinary temperature pH	Slow ageing for 4 months pH.	Rapid ageing by heating pH.
A	5.08	5.78	6.79
B	6.63	7.06	7.28
C	7.29	7.32	7.43

It is found that the hydrated oxide sample C behaves as iso-electric in the alkaline region where as the other samples have their iso-electric points in the acidic region. It is observed that in all the cases these iso-electric points shift towards the alkaline region on ageing.

From the above table it becomes clear that the hydrated oxide samples A, B and C behave differently in their character. The sample A is capable of adsorbing the anions of the acid dyes only when the medium is slightly acidic whilst the sample C is capable to do so even in the neutral medium pH 7. The sample B lies intermediate between the samples A and C. It should be recalled that sample A has more acidic character which is to be suppressed in slightly acidic medium before it is capable of adsorbing the anion of a dyestuff. The sample A, precipitated with excess alkali has been found to possess a good adsorptive capacity for the cations. Sample C as we have already shown (1) possesses a good adsorptive capacity for the anions because of its predominantly basic character and it is found to be associated with fair amount of  $\text{Cl}^-$  ions during the course of its preparation.

It is seen that with ageing of the hydrated oxide either by keeping it for a longer period in water or by warming it, the iso-electric points shift towards the alkaline region. This indicates the variations in the nature of the solid surface with age and it is interesting to conclude that the acidic character of hydrated aluminium oxide quickly decreases than its basic property. This is in line with my observations already made with the different samples that the ageing to more rapid for the sample A which has more acidic behaviour.

Further work on hydrous oxides is in progress in this laboratory which will form the subject-matter of subsequent communications.

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## A NOTE ON THE MECHANISM OF AGEING OF HYDROUS OXIDES.

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Hydrous oxides are known to undergo remarkable changes with ageing which is accompanied by variations in physical and chemical properties. Lottermoser (1) investigated the ageing of hydrous oxides of aluminium, chromium, iron, nickel and cobalt by X-ray studies and concluded that with increase in age there is (a) the growth of secondary particles and (b) change of orientation of the structural units of the secondary particles. Studies with hydrous chromium oxide were also done by Gjaldback (2) who observed the decrease in solubility with age and ascribed it to the difference in particle size. Fricke (3) observed no significant change in the X-radiogram with ageing. It was found by Fricke and Windahausen (4) that ageing of chromium hydroxide is more rapid under alkali solutions.

While in general it is known that there is a diminution of chemical activity of most of the insoluble hydrous oxides with age, not much information is available regarding the mechanism of ageing. In our studies with hydrous chromium and aluminium oxides we have investigated the variations in the surface activity of the hydrous oxides by noting the changes in the extent of adsorption by the hydrous oxide. We have prepared three samples A, B and C of the hydrous oxide by the interaction of the soluble chlorides using 10% excess, equivalent and 10% deficient alkali respectively. The samples have been washed with distilled water to free them from electrolytes. The adsorption by the hydrous oxide suspended in water of various cations and anions and also of basic and acidic dye-stuffs have been studied. The general observation that the surface activity diminishes with age has been corroborated by Tewari and Ghosh (5), where it has been shown that the extent of adsorption decreases with the progressive age of the sample. It will be of interest to compare certain typical results computed from the experimental tables (6) to show the effect of age on the extent of adsorption. The following table summarises the effect of age on the adsorption of various ions by the samples A, B and C of the hydrous chromium oxide.

*Table I.*

*Adsorption by hydrous chromium oxide.*

Percentage decrease of adsorption by 20 days ageing.

Ions.	Sample A.	Sample B.	Sample C.
Cu <sup>++</sup>	24	55	47
Ag <sup>+</sup>	23	35	33

Ba <sup>++</sup>	45	50	55
Methylene-blue	6	14	12
CrO <sub>4</sub> ''	62	42	25
Fe (CN) <sub>6</sub> '''	50	45	38
S <sub>2</sub> O <sub>3</sub> ''	60	47	40
Congo-red	8	6	4

We find from the above table that the effect of ageing is maximum for the adsorption of cations or basic dye-stuffs in the case of sample B, while in the adsorption of anions or acid dye-stuffs the effect of age is maximum in sample A. In the table II we have recorded the effect of age on the adsorption of various ions by the samples of the hydrous aluminium oxide.

Table II.

*Adsorption by hydrous aluminium oxide.*

Percentage decrease of adsorption by 20 days ageing.

Ions.	Sample A.	Sample B.	Sample C.
Cu <sup>++</sup>	38	39	50
Ag <sup>+</sup>	25	35	50
CrO <sub>4</sub> ''	100	80	47
Fe (CN) <sub>6</sub> '''	100	77	47
MnO <sub>4</sub> '	75	40	37
S <sub>2</sub> O <sub>3</sub> ''	75	58	36
C <sub>2</sub> O <sub>4</sub> ''	35	30	28
Orange-II	25	15	10

From the above table it is seen that the maximum decrease of the adsorption of anions takes place in sample A where we find that ageing brings about a remarkable variation in the extent of adsorption. On the other hand the adsorption of cations undergo the greatest decrease with sample C. From these results we find that the ageing of the hydrous oxide has different effects on the adsorption of acidic or basic groups.

The prevalent views on the mechanism of ageing of hydrous oxides suggest a diminution of the surface activity, loss of hydration and chemical reactivity. From our results, while agreeing on the decrease of surface activity we find that the adsorption does not depend entirely on the surface-activity. Ageing of the hydrous oxide seems to have different effect on the adsorption of acidic and basic groups depending on the character of the hydrous oxide precipitated *e.g.*, we find that the adsorption of basic groups by sample B of hydrous chromium oxide shows maximum ageing effect while with acidic groups sample A of the hydrous chromium oxide

shows maximum ageing effect. These results conclusively establish that though the surface-activity diminishes with age, no further generalisation is possible to explain the effect of age on such amphoteric hydrous oxides, where some sort of chemical interaction is responsible for the changes in its adsorptive capacity with age. These results, therefore, again conclusively prove the great part played on the adsorptive capacity of the hydrated chromium oxide on the conditions of its precipitation.

In our studies (7) with amphoteric hydrous oxides we have advanced certain chemical equations to explain the reactions of the hydrous oxides. We have definitely established that the acidic and the basic properties of the amphoteric oxides can be controlled by the conditions of precipitation. We have also shown that hydration and particle size of the hydrous oxide are intimately connected with the amount of alkali employed for precipitation and the temperature of the reaction. In a paper we (8) have conclusively shown in connection with the studies with nickelous hydroxide that particle size has little effect on the solubility of the oxide in ammonia solution. It appears, therefore, that the changes observed in the hydrous oxide on ageing are not so much dependent on particle size, hydration, etc. as on the orientation of the molecules within the particles. These orientations are effected by the mutual neutralization of the acidic and basic properties of the hydrous oxide which consequently effects the hydration and particle size. Thus it is natural that samples of an amphoteric oxide having different acidic or basic properties should behave differently after ageing towards the adsorption of cations and anions.

It must be stated here that the percentage decrease of the adsorption of cations and anions for the various samples A, B and C for hydrous chromium oxide is not in a regular decreasing order and that the sample B of hydrous oxide ages more quickly than the sample C for the adsorption of both cations and anions. The sample B, however, has shown amorphous character by X-ray analysis and usually possessed greatest adsorptive capacity for both cations and anions. It appears, therefore, that the ageing effect on sample B is due to its different physical form.

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